Chemical Reviews

The Photochemistry and Spectroscopy of β,γ-Unsaturated Carbonyl Compounds

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I. Introduction

A. Scope and Organization

Although the growth of knowledge about β,γ-unsaturated carbonyl photochemistry has occurred during a span of barely 15 years, a substantial trunk of fact embellished with a healthy foliage of speculation now flourishes concerning this area of chemistry. The allure of β,γ-unsaturated carbonyls to photochemists, spectroscopists, and theoreticians can be attributed to the proximal incorporation of the alkene and carbonyl chromophores in these molecules. These materials serve as sources of information about either energy transfer between the individual chromophores or, alternatively, about orbital or state interactions between these chromophores and reactions of the excited states of these composite chromophores.

This review is, first, an attempt to organize the massive "trunk" of photochemical fact along structural lines and, second, to relate these facts to spectroscopic and theoretical observations. Finally, an attempt to prune the speculative foliage in order to promote the rapid growth of the field has been attempted.

The literature coverage is believed to be complete through 1973, and most references appearing through September of 1974 are included.

B. Introductory Survey

The β,γ-unsaturated ketones and other types of β,γ-unsaturated carbonyl compounds undergo virtually all of the photochemical reactions known for isolated ketones or alk-
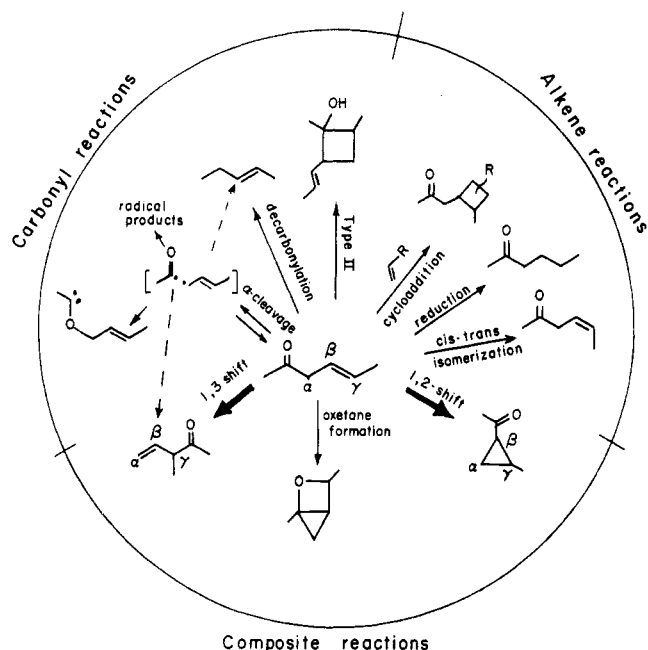
Composite reactions

Figure 1. Reactions of β,γ-unsaturated carbonyl compounds.

enes, and several unique reactions as well. As shown in Figure 1, the reactions characteristic of ketones include α-cleavage, decarbonylation, and type II reactions, while the alkene-like photochemical reactions include [2 + 2] cycloadditions, reductions, and cis,trans isomerizations. Aside from intramolecular oxetane formation, for which intermolecular precedents abound, the presence of both chromophores in a single molecule leads to two unique reactions: the 1,3-shift (the earliest discovered photochemical reaction of β,γ-unsaturated ketones) and the 1,2-shift or oxa-di-π-methane rearrangement.

Much of the known photochemistry of β,γ-unsaturated carbonyls is dominated by 1,3-shifts occurring from excited singlet states and 1,2-shifts occurring from excited triplet states. The mechanisms of these reactions, the nonoccurrence of intersystem crossing in many β,γ-unsaturated carbonyls, and the intense $n\pi^*$ absorptions and "charge transfer" transitions observed in the electronic absorption spectra of these species are the unique features of these compounds which have attracted the most interest and can be understood only by a cooperative interplay of photochemical, spectroscopic, and theoretical principles.

In section II, the photochemistry of β,γ-unsaturated carbonyl compounds is reviewed. The organization is based on structures of the compounds, and the experimental data and interpretations by the original authors are given, accompanied by minimal intrusions by the reviewer. A comprehensive critical examination of the data in terms of modern theoretical concepts is reserved for section IV.

II. Photochemistry

A. Bicyclo[3.2.0]hept-6-en-2-ones

The first photochemical reaction of a β,γ-unsaturated ketone was discovered by Büchi and Burgess in 1960.[1] A photostationary state between **1a** and **2a** (4.5:1 in Pyrex) was formed upon irradiation of either **1a** or **2a**. The forerunner of a concerted 1,3-sigmatropic shift mechanism was proposed for this reaction.

Schuster and Sussman measured a quantum yield of 0.041 for the conversion of **1a** to **2a**.[2] Although these authors also reported that formation of **2a** could be sensitized,[2,3] Ipaktschi reported that acetone-sensitized photolysis of **1a** gave **3a**,

	R_1	R_4	R_6	R_7
a:	Me	Me	H	H
b:	H	H	H	H
c:	H	H	Me	Me
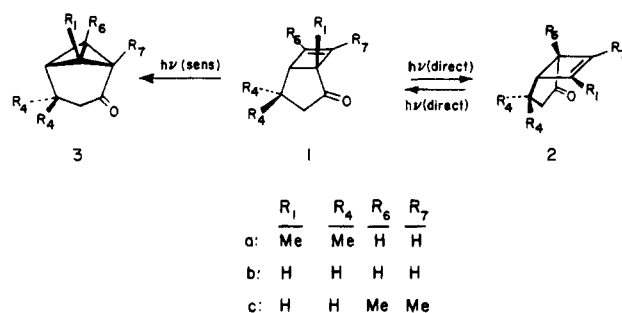
the result of a 1,2-shift, and none of the 1,3-shift product **2a**.[4,5] Photolysis in benzene also gave some **3a**, in a reaction which could be quenched by piperylene. An unusual 1,2-shift upon direct photolysis is implicated. The parent [3.2.0] system **1b**, for which the 1,3-shift is undetectable in the absence of labels, also undergoes the 1,2-shift (**3b**) on acetone-sensitized photolysis.[5] The 2-butyne:cyclopentenone photoadduct **1c** undergoes a photochemically reversible 1,3-shift upon direct irradiation to give a photostationary state of **1c** and **2c** in a ratio of 1.5–2:1.[6,7] Sensitized irradiations of **1c** have not been reported.

Cargill and coworkers have observed a number of 1,3-shifts as well as reductions and cycloadditions in tricyclic propellane systems.[8-11] Thus, **4a** and **5a** form a 1:2.3 photostationary state upon direct irradiation,[8] while **4b** and **5b** give a 1:2 photostationary state.[9] The first report[8] of this latter reaction also mentions the formation of the 1,3-hydrogen shift product **6** upon irradiation of **4b**. The unsubstituted [3.3.2.0]

	R	n
a:	Me	6
b:	Me	5
c:	H	5
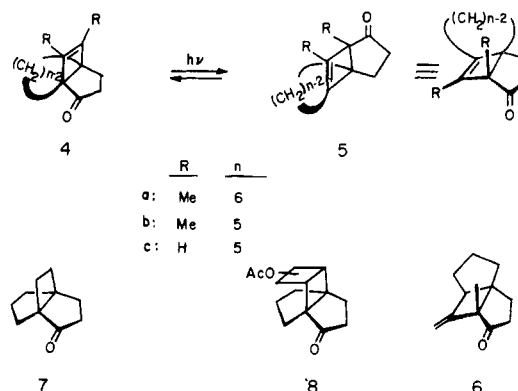
system **4c** undergoes a 1,3-shift upon irradiation in pentane, but only the photoreduction product **7** can be isolated.[9] Irradiation of **4c** in methylene chloride produces **7** along with tetrachloroethane,[10] while in the presence of vinyl acetate, **4c** undergoes a photocycloaddition to form **8**.[10]

Photocycloaddition of 2-butyne to bicyclo[3.2.0]hept-3-en-2-one gives a mixture **9a, 9b, 10a,** and **10b**.[11] This was interpreted as the result of photochemical 1,3-shifts from the initial adducts **9a** and **10b**. A photostationary state (2.7:1) was observed between **9a** and **10a**. Irradiation of **9c** resulted in the photochemical reduction of the double bond in the 1,3-shift isomer **10c**. The dienes **11a** and **11b** form homocubanones upon direct irradiation, most likely via the 1,3-shift in-
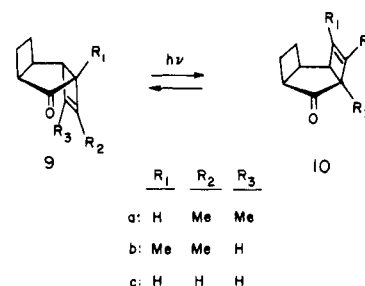
	R_1	R_2	R_3
a:	H	Me	Me
b:	Me	Me	H
c:	H	H	H

TABLE I. Ultraviolet Spectra of
Bicyclo[3.2.0]hept-6-en-2-ones

Compd	λ_{max}, nm (ϵ)		Solvent	Ref
1a	219(820)	303(174)	EtOH	1
2a	219(1730)	303(230)	EtOH	1
1c		304(327)		6
2c		305(243)		6
4a		307(340)	EtOH	8
5a		310(460)	EtOH	8
4b		307(210)	EtOH	8
4c		307(101)	EtOH	10
6		304(170)	EtOH	8
9a		311(349)	95% EtOH	11
10a		319(140)	95% EtOH	11
9b		310(229)	95% EtOH	11
10b		309(301)	95% EtOH	11
9c		310(102)	95% EtOH	11
10c		310(146)	95% EtOH	11
11a		306(267)	95% EtOH	11, 12
11b		309(323)	95% EtOH	11, 12

termediates, **12**, which undergo intramolecular [2 + 2] cycloadditions to form the caged products. Cargill and coworkers suggested that energy transfer from the carbonyl to the double bond occurs, followed by intramolecular cycloaddition of the excited alkene.[12,13] Yano found that acetone-sensitized photolysis of **11a** gives the thermally labile **13**.[14] The compound is unchanged upon further photolysis.
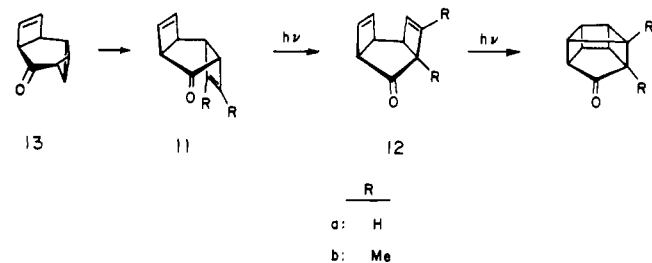
The ultraviolet spectra reported for the bicyclo[3.2.0]hept-6-en-2-ones discussed here are given in Table I. These compounds all have enhanced $n\pi^*$ absorptions at 303–319 nm with extinction coefficients of 100–460. Each alkyl substituent on the alkene increases ϵ by a factor of 1.5–2, but the position of λ_{max} is found to be solvent insensitive.

B. Bicyclo[4.2.0]oct-7-en-2-ones

Cargill and coworkers have found that the propellanes incorporating this ring system, **14a** and **14b,** undergo clean, but different, photochemical reactions upon direct irradiation. Thus, **14a** undergoes photoreduction of the double bond (**15**), while **14b** gives a 1,3-hydrogen shift.[13] Cargill proposed that β,γ-unsaturated ketones with ϵ_{max} greater than 150 (reflecting strong carbonyl–alkene interaction) undergo 1,3-acyl
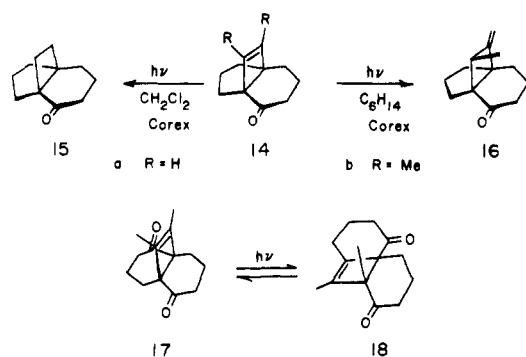
TABLE II. Ultraviolet Spectra of
Bicyclo[4.2.0]oct-7-en-2-ones

Compd	λ_{max} (ϵ)		Solvent	Ref
14a		296(85)		13
14b		296(168)		13
17	230(3640)	299(472)	95% EtOH	15

shifts, while those with smaller ϵ_{max}'s undergo reactions characteristic of isolated chromophores.[13] The β,γ-unsaturated diketone **17** gives a reversible 1,3-shift to form **18**.[15] A photostationary state of **17** and **18** in a 1:3 ratio is formed in hexane.

The ultraviolet spectra of these compounds are given in Table II. Once again, the effect of alkene alkylation can be seen in the extinction coefficients. The 5-endo-methyl analog of **17** was also synthesized.[15] This compound has an approximately ten times larger ϵ_{max} than the saturated analog.

C. Bicyclo[3.2.0]hept-2-en-7-ones and Bicyclo[2.2.1]hept-5-en-2-ones (2-Norbornenones)

The photochemistry of dehydronorcamphor (5-norbornen-2-one, **19**) was studied independently by the groups of Schenck[16] and Schuster.[17] Schenck reported that the quantitative photolytic fragmentation of **19** to ketene and cyclopentadiene occurred in a variety of solvents at temperatures from −70 to 25° with a quantum yield of 0.25.[16] Schuster et al. found that the 1,3-shift product **20** was formed rapidly, and ketene and cyclopentadiene were formed more slowly.[17]
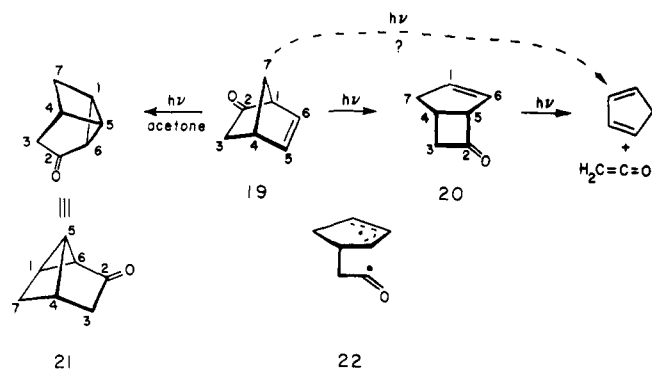
Most, if not all, of the ketene and cyclopentadiene arises from **20**. Both groups proposed diradical **22** as an intermediate in these reactions. Ipaktschi reported that acetone-sensitized photolysis of **19** led mainly to the 1,2-shift product **21** accompanied by a small amount of the 1,3-shift product and several unidentified hydrocarbons.[18]

Schexnayder and Engel confirmed the formation of both **20** and **21** upon sensitized photolysis. The quantum yields for formation of **20** and **21** are 0.18 and 0.16 with acetone as sensitizer, 0.013 and 0.13 with acetophenone, and 0.006 and 0.042 with benzophenone as sensitizer. Furthermore **20** is converted into **21** upon acetone-sensitized photolysis.[18a] This result emphasizes that caution should be exercised in interpreting sensitized reactions which give only 1,2-shift products, because 1,3-shift isomers can both give the same 1,2-shift product.

Cookson and Bays reported on the direct photolysis of the optically active 2-norbornenones **23**.[19] In each case, both the 1,3-shift products **24** and the cyclopentadienes and ketene were formed.

In a detailed study of the photochemistry of verbenone, Erman reported that one of the minor verbenone photoproducts, **25**, underwent a number of photoreactions, which were rationalized as shown in the drawing.[20] In methanol, **34** (5%),

	R_1	R_2	R_3
a:	Me	H	H
b:	H	Me	H (enantiomer)
c:	Me	H	Ph (enantiomer)
d:	H	Me	Ph
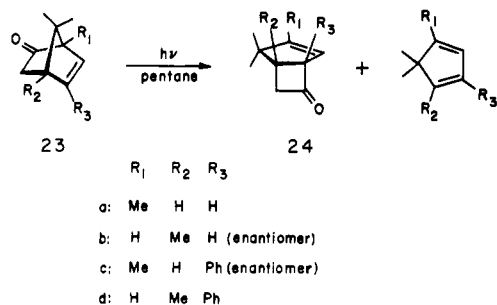
ketals **28** (5%) and **30** (11%), and an unidentified aldehyde (14%) were formed. In cyclohexane, or benzene, **32** (1.8%), **33** (2.1%), and hydrocarbon **29** (12%) were found along with numerous other products in small yields. The results could be rationalized by assuming formation of the isomeric diradicals **26** and **27** in the primary photochemical process.[20]
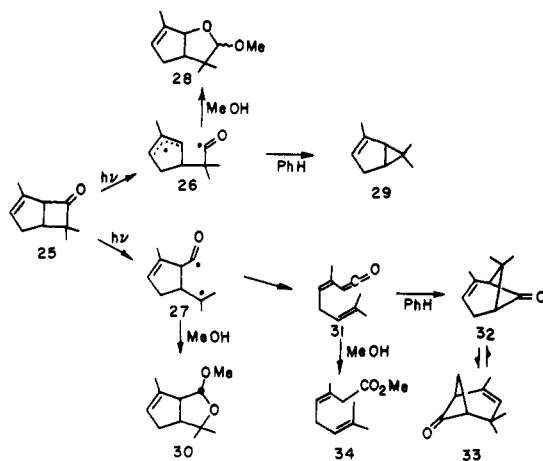
Similarly complex photochemistry was observed in the study of 3,3-dimethoxy-5-norbornen-2-one (**35**).[21] Photolysis in hydrocarbons, dioxane, acetone, or acetonitrile gave the decarbonylation product **39**, in 80% yield, accompanied by the 1,3-shift product **38**, whose concentration rapidly reached a maximum and then decreased at the expense of decarbonylation. Irradiation in methanol gave epimeric acetals **40**, along with **38** and **39**. Photolysis at −50° in methylcyclohex-

ane resulted in faster disappearance of **35**, faster appearance of **38**, and slower appearance of **39** than at 25°. The maximum yield of **38** varied from 70% at −80° to 30% at 40°. Sharf and Küsters suggested a mechanism involving α-cleavage as the primary photochemical process, followed by partitioning of the diradical **36** between formation of oxacarbene **37** (which was trapped only in methanol), 1,3-shift product **38**, and decarbonylation product **39**.[21] The temperature
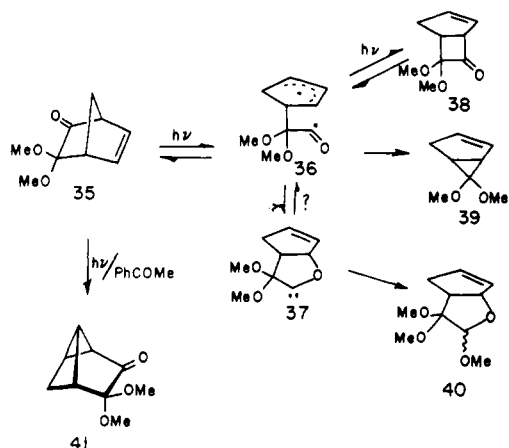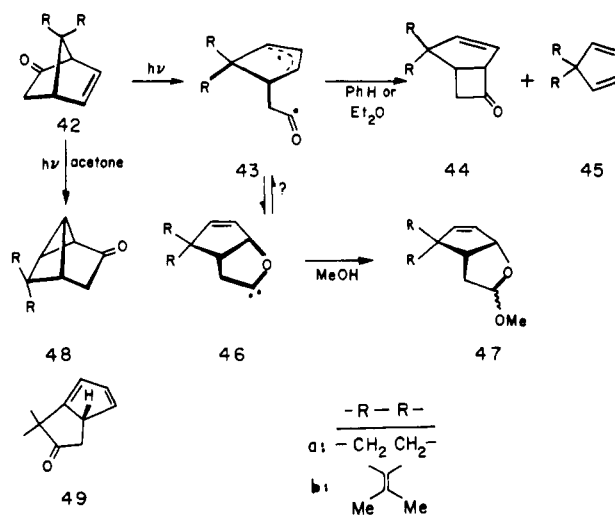
dependence indicated that **36** was a discrete intermediate with a small energy barrier toward decarbonylation. The greater efficiency of disappearance of **35** at low temperature could mean either that radiationless deactivation of the excited singlet of **35** was less efficient at low temperature, or that there is a smaller barrier for loss of CO from **36** than for reclosure of **36** to **35**.

Recent theoretical considerations[22] suggest that **37** may be formed directly from **38**, while **36** will be formed from **35**. This hypothesis is discussed in more detail in section IV.

Scharf and Küsters reported that the conversion of **35** to **38** and **39** was neither quenched by piperylene and 1,3-cyclohexadiene nor sensitized by acetone or benzophenone. However, a different product, tentatively identified as the 1,2-shift product, **41**, was formed upon acetophenone-sensitized photolysis.[21]

Ipaktschi reported similar photochemistry for the spiro-2-norbornenone **42a**.[18,23] Upon direct photolysis of **42a** in ether or benzene, the 1,3-shift product **44a** (52%) and spirodiene **45a** (17%) were formed.[23] Irradiation of **42** in methanol gave the epimeric acetals **47**. Neither of these reactions was affected by added piperylene, indicating that a singlet excited state leads to diradical **43a**, whose behavior is analogous to that of **36**, except that loss of ketene replaces decarbonylation as one of the reaction paths. The irradiation of a 0.02 M solution of **42a** in acetone gave the 1,2-shift product **48a**, whose formation was quenched by piperylene. Photolysis of a 0.3 M solution in acetone gave both 1,2- and 1,3-shift products. This result indicates that the formation of **48a** in ace-

tone solvent is the result of triplet energy transfer from acetone, because under conditions where light is absorbed directly by **42a** in acetone solution, the normal singlet product **44a** is formed.[23] The bis(β,γ-unsaturated) ketone **42b** gave only **44b** and dimethylfulvene, **45b**, upon direct irradiation, even though the alternative product **49** could have been formed by a 1,3-shift.[23] Kinetic effects most likely dictate the formation of **45b** rather than **49**, because the benzo analog **50** readily gives the 1,3-shift product **51**, analogous to **49**.[23]
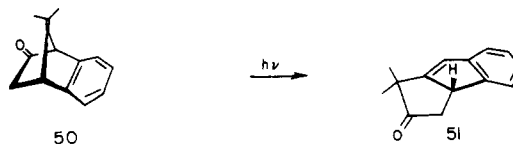
Acetone-sensitized irradiation of **42b** gives **48b**, which could arise either from an oxa-di-π-methane rearrangement involving the endocyclic double bond, or from a di-π-methane rearrangement involving the 1,4-diene moiety. Since the alcohol corresponding to **42b** is photochemically unreactive, Ip-

TABLE III. Ultraviolet Spectra of Bicyclo[3.2.0]hept-2-en-7-ones

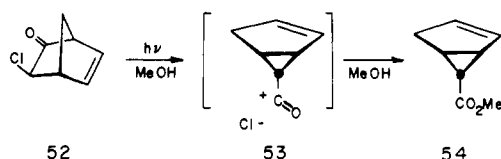| Compd	λ_{max}, nm (ϵ)		Solvent	Ref
	$\pi\pi^*$	$n\pi^*$		
20*		284(>73), 297(>142), 306(>160), 317(>112)	C_8H_{18}	17
1-Me-20		302(290)	EtOH	23
6-Me-20		301(340)	EtOH	23
7-Me-20		302(310)	EtOH	23
24a		297(222), 306(238), sh315(169)	C_6H_{12}	19
	sh224(2100)	302(285)	95% EtOH	19
24b		292(170), 307(190), 318(135)	C_6H_{12}	19
24c	sh217(15700), 261(327)	sh303(518), 310(610), sh321(476)	C_6H_{12}	19
	sh217(10400), 261(280)	310(710)	95% EtOH	19
24d	sh211(11850), 260(258)	301(366), 310(425), 331(300)	C_6H_{12}	19
	sh215(12700), 260(302)	306(470)	95% EtOH	19
25		307(289)	$CHCl_3$	a
38		sh320(115), 331(143), 344(116)	C_6H_{14}	21
44a		296(225), 308(250), 318(165)	C_6H_{12}	23
44b	250(9500)	297(670), 307(670), 319(430)	C_6H_{12}	23
1,4,4-Me$_3$		307(253)	C_6H_{12}	b

^{a} W. F. Erman, R. S. Trepton, P. Bazukis, and E. Wenkert, *J. Am. Chem. Soc.*, **93**, 657 (1971). ^{b} H. Hart and T. Takins, *ibid.*, **93**, 720 (1971).

aktschi suggested that the oxa-di-π-methane mechanism occurred.[23]

Four monomethyl-2-norbornenones have recently been photolyzed to give the corresponding 1,3-shift products.[24]

A photochemical solvolysis is observed upon irradiation of *exo*-3-chloro-5-norbornen-2-one in methanol.[25] Thus, **54** is formed with a quantum yield of 0.8. Since the reaction could be neither quenched by piperylene nor sensitized by acetophenone, Kaplan and Hartwig proposed that ionization of the excited singlet to intermediate **53** occurred.[25] Givens and co-workers have reported similar reactions of *exo*-3-chlorobicyclo[2.2.2]oct-5-en-2-one. The quantum yield of the "photo-

chemical solvolysis" is 0.12 for the exo compound and less than 0.01 for the endo, indicating some involvement of backside assistance by the double bond in the excited singlet state. Flash photolysis studies gave no evidence for formation of chlorine atoms in these systems, but an initial homolysis seems probable to the authors of this report.[26]

The heterocyclic bicyclo[3.2.0]hept-2-en-7-one, **55**, undergoes photochemical reactions which can all be rationalized by primary formation of the α-cleavage diradical **56**, followed by both decarbonylation (8%) and ketene loss (24%).[27]
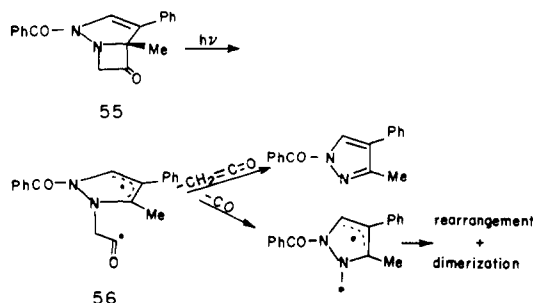
Although the intervention of a diradical in the 1,3-shift mechanism is not unequivocal, the 2-norbornenone and bicyclo[3.2.0]hept-2-en-7-ones clearly undergo α-cleavage, and

there is some evidence (Scharf and Küsters)[21] for the common intermediacy of the acyl–allyl diradical in formation of all the singlet products. No 1,3-shifts of the [3.2.0] systems to the norbornenone systems have been observed, suggesting that the acyl–allyl diradical, if formed, does not cyclize to the norbornenone system.

Ultraviolet spectral data for the systems discussed in this section are given in Tables III and IV. For the bicyclo-[4.2.0]hept-2-en-7-ones (Table III), vibrational structure ($\sim$1300 cm^{-1}) is observed in the nπ^* absorptions in nonpolar solvents, and the ϵ_{max}'s are about three times those of saturated analogs.[21] Although vibrational structure disappears in polar solvents, the values of λ_{max} and ϵ do not change significantly. For the compounds lacking a γ-phenyl, which is expected to further enhance nπ^* absorptions (see later), the normal range of λ_{max} is 305–308 nm and of ϵ_{max} is 112–250. The dimethoxy compound has a much larger ϵ.

The 2-norbornenones (Table IV) have nπ^* absorption maxima at about 309 nm with ϵ's of about 300, unless the alkene is substituted with an aromatic ring. In the latter cases, both bathochromic shifts and large intensifications are observed.

D. Bicyclo[4.2.0]oct-2-en-8-ones and Bicyclo[2.2.2]octenones

The parent system **57** has been studied by Givens and Oettle.[29] Direct irradiation of **57** in ether gave the 1,3-shift product **58**, which, upon further irradiation, lost ketene without any detectable reverse 1,3-shift. Assuming that diradical **59** is an
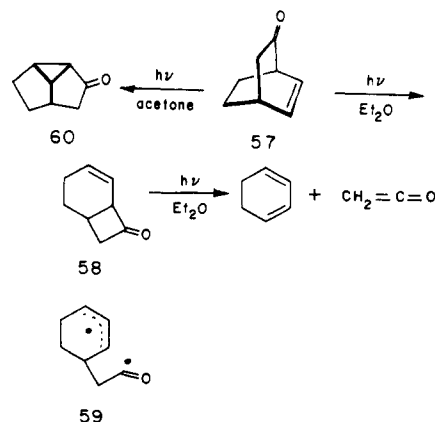
TABLE IV. Ultraviolet Spectra of Bicyclo[2.2.1]hept-5-en-2-ones (2-Norbornenones)

Compound	λ_{max}, nm (ϵ)		Solvent	Ref
	$\pi\pi^*$	$n\pi^*$		
19		sh287.5(162), 296.5(242), 307.5(277), 319.5(177)	C_8H_{18}	9
	210(3000)	308(290)	EtOH	b
23a	216(2440)	307(303)	C_6H_{12}	b
	216(2425)	304(308)	95% EtOH	b
23b	216(2720)	310(325)	C_6H_{12}	b
	216(2660)	303(330)	95% EtOH	b
23c	265(15400), 274(14900)	318(6170), 330(5150)	C_6H_{12}	b
	264(14700), 274(14400)	315(6070)	95% EtOH	b
p-Me-23c	266(16100), 274(16100)	315(6250), 328(5340)	C_6H_{12}	b
p-MeO-23c	sh272(17400), 279(19600)	318(7570), 330(6870)		
23d	255(10400)	315(2560)	C_6H_{12}	b
	254(10700)	315(2830)	95% EtOH	b
p-MeO-23d	265(12650)	312(4640)	95% EtOH	b
35		323(172), sh330(143)	C_6H_{14}	21
42a		295(200), 307(250), 318(170)	C_6H_{12}	23
42b		sh290(228), 301(377), 311(485), 324(334)	C_8H_{18}	a

[a] A. Moscowitz, K. Mislow, M. A. W. Glass, and D. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962). [b] D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. B*, 215 (1967).
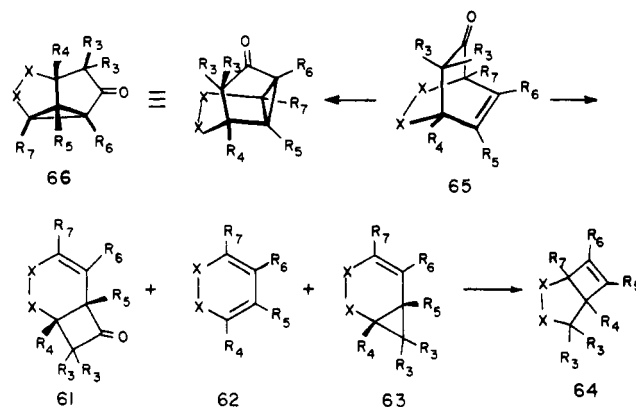
intermediate in the loss of ketene from **58**, these workers concluded that the 1,3-shift is a concerted reaction.[29] However, an alternative explanation could be that diradical **59** is formed from excited singlets of both **57** and **58**, but that the conversion of **59** to **58** is fast, that to ketene plus cyclohexadiene is slow, and cyclization to **57** is uncompetitive with the other processes. Such a mechanism would conform to those suggested for systems discussed earlier. Acetone-sensitized photolysis of **57** gives the 1,2-shift product **60**, implicating a triplet excited state for this reaction and a singlet excited state for the 1,3-shift. Sensitized photolysis of **60** gives only ketene and cyclohexadiene.[29] The heavily substituted bicyclo[2.2.2]octenones **65** undergo the same reactions as the parent, except that decarbonylation is sometimes observed.[28-34] The resulting norcarenes **63** are frequently not isolated, since rapid photoisomerization to **64** occurs. The last reaction formally involves sequential 1,5- and 1,3-shifts.

Compounds of this type which can produce aromatic compounds upon loss of ketene or other stable entities do so readily upon direct irradiation.[29,28] For example, **65a** was irradiated to give the benzene derivative **62** and dimethylketene, and even at $-100°$ none of the 1,3-shift product **61a** could be detected.[30] Similarly, **65b** gave only loss of ketene to form **62b** in good yield.[30] The azodicarboxylate adduct **65c** behaved differently, giving both an isolable 1,3-shift product **61c** and the decarbonylated compound **63c** upon direct irradiation.[32] Since the ratio of **61c:63c** was high after brief irradiation and decreased upon further irradiation, most, if not all, of the decarbonylation arises from **61c**.

Acetone-sensitized photolysis of **65c** gave 91% of the 1,2-shift product **66c**, along with small amounts of singlet products **61c** and **63c**, while acetone-sensitized photolysis of **61c** gave decarbonylation (**63c**) and the 1,2-shift product (**66c**).[32] Hart and coworkers suggested that a reversible 1,3-shift occurred from an $n\pi^*$ singlet, while the decarbonylation and 1,2-shift involved triplet $n\pi^*$ states.[32]

The benzo analog **65d** loses dimethylketene in 82% yield (**62d**) and gives a new decarbonylated product (**64d**) in 13% yield.[30] The benzonorcaradiene **63d** is a likely intermediate in the formation of **64d**. Photolysis in acetone gave 26% of the 1,2-shift product **66d**, and the direct irradiation products **62d** and **64d** in 45 and 6% yield, respectively.[31] The bridgehead demethylated analog **65e** gave a similar product distribution in the acetone-sensitized photolysis.[31]

Direct irradiations of bridged α-diketones or their monoimines, **65l-l**, gave aromatic compounds, **62l-l**, by loss of two

\ X—X /	R_3	R_4	R_5	R_6	R_7
a: MeO₂C⟩=⟨CO₂Me	Me	Me	Me	Me	Me
b: Ph⟩=⟨Ph	Me	Me	Me	Me	Me
c: MeO₂C⟩N—N⟨CO₂Me	Me	Me	Me	Me	Me
d: (benzo)	Me	Me	Me	Me	Me
e: benzo	Me	H	Me	Me	H
f: benzo	H	H	H	H	H
g: benzo	D	H	H	H	H
h: benzo	H	H	D	D	H
i: benzo =NPr	H	H	H	H
j: benzo =N-C-C₆H₁₁	H	H	H	H
k: benzo =NPh	H	H	H	H
l: benzo =NOH	H	H	H	H

carbon monoxides, or CO and an isocyanide, respectively.[35]

The parent benzo system **65f** was studied independently by two groups. Ipaktschi found that direct irradiation of **65f** gave naphthalene **62f** and ketene, while acetone sensitization resulted in formation of naphthalene **62f** (20%) and the 1,2-shift product **66f** (70%).[33] Loss of ketene was suggested to involve a primary α-cleavage.

TABLE V. Quantum Yields of Reactions of 65f

Conditions	Φ_{-65f}	Φ_{62f}	Φ_{61f}	Φ_{66f}
300 nm/Pyrex/PhH	0.50	0.45	0.10	
254 nm/Me$_2$CO(E_T = 79.5)	0.12	0.05		0.05
450 W/PhCOMe(E_T = 74)	0.14	0.01		0.12
450 W/Ph$_2$CO(E_T = 68)	Small			

TABLE VI. Quantum Yields of Reactions of Lactone 67[28,34]

Conditions	Φ_{-67}	Φ_{CO_2}	Φ_{65f}	Φ_{61f}	Φ_{62f}	Φ_{66f}
254 nm/PhH	0.175	0.148	0.020	0.001	0.046	0.061
300 nm/dioxane			0.029	0.002	0.041	0.060

TABLE VII. Ultraviolet Spectra of Bicyclo[4.2.0]oct-2-en-8-ones

Compd	λ_{max}, nm (ϵ)		Solvent	Ref
61c	210(6425)	311(156)	C$_6$H$_{12}$	32
61f	221(22000), 227(19800), 265(8100), 273(8300)		C$_6$H$_{12}$	28

More extensive studies by Givens and Oettle showed that **61f** could be isolated along with naphthalene upon irradiation of **65f** in Pyrex.[29,34,28] Furthermore, sensitized irradiation of the dideuterated compounds **65g** and **65h** gave the oxa-di-π-methane rearrangement products **66g** and **66h**, respectively, rather than the di-π-methane products, which would have different deuterium labeling patterns.

Givens et al. measured the quantum yields for both the direct and sensitized irradiations of **65f**.[28,34] The results of those studies are given in Table V.

Both the direct and sensitized reactions are quite efficient, but intersystem crossing is inefficient or considerably slower than singlet reactions in **65f**. The failure of benzophenone (E_T = 68 kcal/mol) to sensitize the reaction indicates a triplet energy of about 72 kcal/mol for **65f**.[34]

In a study designed to determine whether diradical **68** is involved in the formation of **66f** from sensitized photolysis of **65f**, Givens et al. studied the photolysis of lactone **67**, which was presumed to give **68** upon photolysis.[28,34] Photolysis forms **65f** as well as all of the products formed from direct or
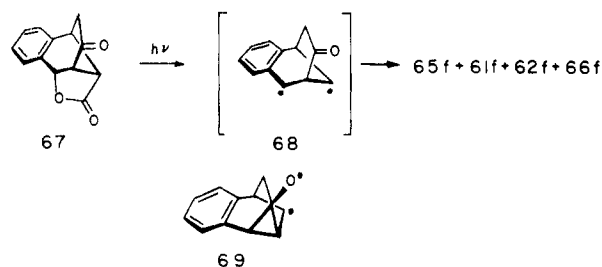

$$67 \xrightarrow{h\nu} [\ 68\ ] \longrightarrow 65f + 61f + 62f + 66f$$

69

sensitized irradiation of **65f**. However, the ratios of the quantum yields for formation of the various products from **67** (Table VI) are very different from those found for **65f** (Table V). The formation of all products from **67** could be quenched by 1,3-cyclohexadiene with equal efficiency, indicating that the same triplet state of **67** leads to all the products. Stern–Volmer kinetics indicate that the quenchable triplet has a lifetime of 20 nsec.[34] Thus, diradical **68** is not involved in photolysis of **65f**, and a concerted mechanism for the 1,2-shift was proposed.[34] However, the involvement of another likely diradical intermediate, **69**, was not ruled out. Givens' experiment does indicate that **69**, if formed, must pass directly to **66f** without passing through a long-lived diradical **68**.

The ultraviolet spectra of the compounds discussed in this section are given in Tables VII and VIII.

E. Bicyclo[3.n.1]alkan-2-en-(6 + n)-ones (2,6-Bridged-3-cyclohexenones)

A study of the photochemistry of chrysanthenone, the 1,3-alkyl shift photoisomer of verbenone,[36] was carried out by Erman.[20] Irradiation of (−)-chrysanthenone (**70**) resulted in rapid and photoreversible formation of (+)-**71**, while extended
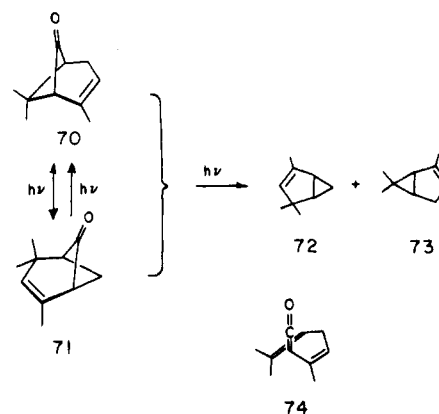
irradiation gave the decarbonylated products **72**, and **73**. The accompanying photoracemization of **70** was thought to involve the ketene **74**.[20]

Erman and Kretschmar reported that the bridged 3-cyclohexenones **75a** and **75b** formed photostationary states with cyclobutanones, **76a** and **76b**, composed of 75a:76a = 1:1.7 and 75b:76b = 1:2.[37] Meinwald and Van Vuuren's studies of the photochemistry of **75a** revealed the more complex nature

TABLE VIII. Ultraviolet Spectra of Bicyclo[2.2.2]octenones

| Compound	λ_{max}, nm (ϵ)	Solvent	Ref
57	200, 293(107)	C$_6$H$_{12}$	a
	202(3000), 298(110)	95% EtOH	b
65a	207(4650), 228(4650), 250(3000), 300(433)	EtOH	c
65c	210(6160), 300(429)	95% EtOH	32
65d	220(6200), 273(430), 300(373)	EtOH	c
65e	216(8130), 268(1200), 273(1100), 300(389)	EtOH	c
65f	288(265), 296(359), 306(372), 320(210)	C$_6$H$_{12}$	28

[a] H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959). [b] D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. B*, 215 (1967). [c] H. Hart, private communication.
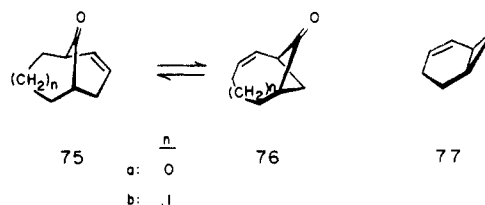
TABLE IX. Ultraviolet Spectra of Bicyclo[3.n.1]alkan-2-en-(6 + n)-ones (2,6-Bridged-3-cyclohexenones) and Their 1,3-Shift Photoproducts

Compound	λ_{max}, nm (ϵ)	Solvent	Ref
70	290(120)	EtOH	36
71	297(180)	EtOH	20
75a	a		37
75b	a		37
76b	299(45)	EtOH	37
Bicyclo[3.2.1]oct-6-en-2-one	212(3600), 299(180)	C_8H_{18}	b

^{a} ϵ_{max} no greater than the corresponding saturated compounds. ^{b} N. A. LeBel, N. D. Ojha, J. R. Menke, and R. J. Newland, J. Org. Chem., 37, 2896 (1972).

of the photochemistry involved.[38] Irradiation (λ >210 nm) of 75a in pentane at 25° led to a rapid build-up of 76a to a maximum of 45%, followed by appearance of decarbonylated compound 77 at the expense of both 75a and 76a. At −60°, more decarbonylation occurred but the maximum concentration of 76a was unchanged. At 25° with a Pyrex filter (λ >300 nm) decarbonylation was suppressed, but the maximum yield of 76a was the same.[38] One possible hypothesis compatible with the wavelength-dependent results is that different excited states are involved in the 1,3-shift and the decarbonylation. However, in the absence of quantum yields, the wavelength- and temperature-dependent results do not exclude a common diradical intermediate for both reactions, as long as different barriers to formation of 75, 76, and 77 exist. In fact, the behavior of 75a is very similar to that of the dimethoxynorbornenone 35 discussed earlier, and the photochemistry of 35 was suggested to involve initial α-cleavage.

The ultraviolet spectra of the systems discussed in this section suggest far weaker interactions of the carbonyl and alkene groups than were present in previously discussed compounds (Table IX).

F. 3-Cycloalkenones and 2-Alkenylcycloalkanones

1. 3-Cyclopentenones and Alkenylcyclopropanones

The behavior of 3-cyclopentenone is anomalous in that neither the possible 1,3-shift or 1,2-shift has been observed in this system (Figure 2). Instead, decarbonylation is the most general photochemical fate of these compounds. For this reason, the 3-cyclopentenones are discussed in a later section of this review. However, Chapman has observed that the vinylcyclopropane 78, which is stable at low temperature, can be photochemically decarbonylated to 79.[39] Thus, the failure to detect photoreactions of 3-cyclopentenones other than decarbonylation may be the result of a failure to search for intermediates.
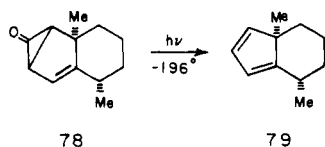
2. 3-Cyclohexenones (Nonbridged) and 2-Alkenylcyclobutanones

A number of the bicyclic classes discussed earlier are disguised examples of reactions of 3-cyclohexenones or of 2-alkenylcyclobutanones. The 2-norbornenes (section II.C), and 2,6-bridged-cyclohexenones (section II.E) are all bridged 3-cyclohexenones. Upon direct irradiation, all of these materials undergo 1,3-shifts to form 2-alkenylcyclobutanones either via, or accompanying, α-cleavage. The 2-alkenylcyclobutanones α-cleave on direct irradiation to give ketene loss, decarbony-
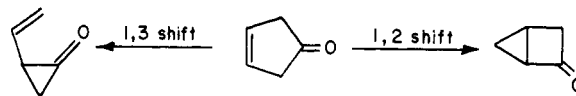
Figure 2. Hypothetical 1,3- and 1,2-shifts of 3-cyclopentenone.

lation, and recombination in several possible ways. For the first two systems of this type, triplet-sensitized irradiation results in 1,2-shifts, while sensitization has apparently been attempted only with 58, which results in ketene loss, presumably via α-cleavage.

The monocyclic or fused 3-cyclohexenones behave somewhat differently from the bicyclic cases in that 1,3-shifts are not always observed. Williams and Ziffer first reported examples of the oxa-di-π-methane rearrangement, or 1,2-shift, upon the direct (unsensitized) irradiation of several β,γ-unsaturated ketones.[40,41] The parent octalone 80a and the steroid 80b underwent 1,2-shifts upon irradiation in tert-butyl alcohol with a Pyrex filter.[40] Benzophenone was found to enhance disappearance of 80b, but only a trace of 81b could be isolated in this reaction,[41,42] while piperylene quenched the reaction of 80b. Both of these reactions were suggested to involve α-cleavage from an excited triplet state of the ketone. Engel found that the quantum yield of formation of 81a was 0.05 in benzene and that the reaction could be sensitized by acetone and quenched by piperylene or 1,3-cyclohexadiene.[43] Williams and Ziffer found that 3-cyclohexenone was unreactive, while the isomeric β,γ-unsaturated ketone 80c added tert-butyl alcohol in preference to the 1,2-shift reaction.[40] Schaffner and coworkers found that the monosubstituted compound 80d also underwent the unsensitized 1,2-shift.[44]
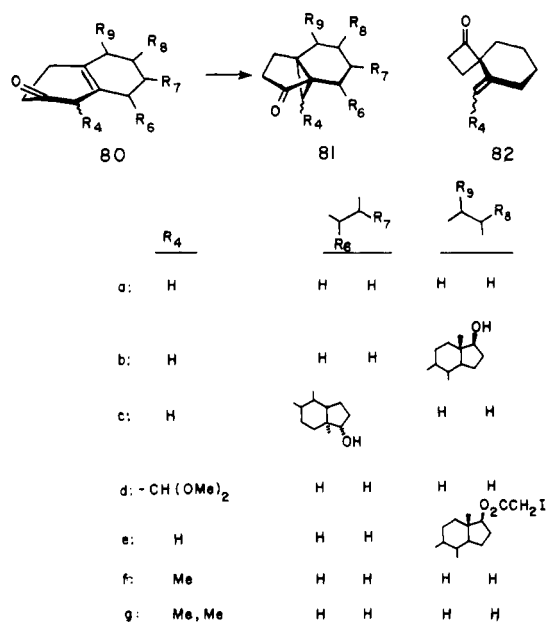
TABLE X. Quantum Yields for Photoreactions of
Octalones 80 at 313 nm

	Direct irradiation			Acetone-sensitized irradiation		
Compd	$\Phi_{-K}{}^a$	Φ_{81}	Φ_{82}	$\Phi_{-K}{}^a$	Φ_{81}	Φ_{82}
80a	0.15	0.05		0.18	0.05	
80f	0.28	0.12	0.15	0.21	0.06	0.01
80g	0.39		0.24	0.06	0.03	

^{a} Ketone disappearance.

Williams and Sarkisian suggested a qualitative explanation for the unusual propensity of the fused 3-cyclohexenones to undergo intersystem crossing and 1,2-shift from the triplet manifold, rather than 1,3-shift from the singlet manifold.[45] These authors suggested that the 1,3-shift proceeds by $\alpha$-cleavage, but that the α-cleavage is rapid relative to intersystem crossing only when the σ bond α to the carbonyl overlaps effectively with the π_{CC} bond.[45] A recent X-ray analysis of a steroidal fused 3-cyclohexenone, **80e**, indicates the "semiplanar" nature of the 3-cyclohexenone ring,[46] in agreement with the Williams and Sarkisian explanation.

Very recently, Engel and Ziffer and their coworkers have found that methylation promotes the rate of 1,3-shift (α-cleavage) with respect to the rate of intersystem crossing.[47] Whereas the parent compound **80a** undergoes only the 1,2-shift upon direct irradiation, the α-methyl derivative **80f** undergoes both 1,2- and 1,3-shifts (**82f**) upon direct irradiation. The α,α-dimethyl derivative **80g** gives only the 1,3-shift products **82g** on direct irradiation and the 1,2-shift product **81g** upon acetone-sensitized irradiation.[47] The quantum yields for these processes are given in Table X. The conversion of **80a** to **81a** was quenched by cis-piperylene, which was isomerized, and the quantum efficiency of intersystem crossing in **80a** was determined to be at least 0.5. The 1,2-shift of **80g** was unaffected by cyclohexadiene. In all three compounds, the 1,3-shift product is formed in a singlet reaction, while the 1,2-shift products are formed by triplet reactions. Engel et al. suggest that α-methylation causes an acceleration of α-cleavage, leading ultimately to 1,3-shift product, and that **80a** and its analogs which undergo 1,2-shifts upon direct irradiation are unusual only in that α-cleavage is less efficient than intersystem crossing.[47]

Fused 3-cyclohexenones, in which the alkene is further conjugated, appear to behave more like other β,γ-unsaturated ketones, as does **80g**. Thus, Nakanishi et al. reported that **80h**, which resembles **80a–g** closely except that the alkene is now conjugated with an aromatic ring, undergoes both a 1,3-shift and decarbonylation upon direct irradiation in tert-butyl alcohol, while acetophenone-sensitized irradiation of **80h** gives a 1,2-shift.[48,49] Nakanishi et al. suggested that the carbonyl group and the alkene interact more strongly in **80h** than in **80a** and its analogs, so that α-cleavage becomes faster than intersystem crossing.[49] Williams studied a $\beta,\gamma,\delta,\epsilon$-unsaturated ketone, **80i**, and found that direct irradiation gave the 2-vinylcyclobutanone **83i**, which decarbonylates upon further irradiation, (**84i**).[50]
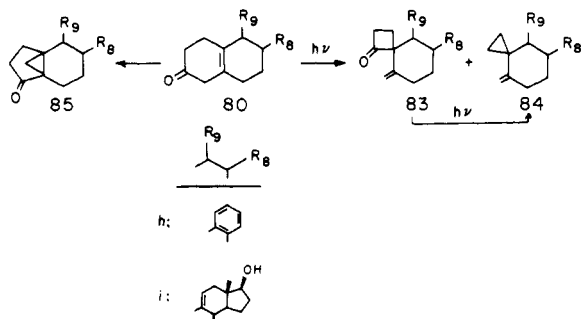

TABLE XI. Ultraviolet Spectra of 3-Cyclohexenones

Compound	λ_{max}, nm (ϵ)	Solvent	Ref
3-Cyclohexenone	277(108)	C_6H_{12}	a
	278(36)	C_6H_{12}	b
80a	281(38)	EtOH	c
	285(19)		
80b	284(34)	MeOH	40
80f	283(70)		47
80g	278(55)		47
80h	224(15400), 262(11700), 267(11400), 292(1200)	MeOH	48
80i	267(900), 275(900)	MeOH	48

^{a} H. Labhart and G. Wagnieré, Helv. Chim. Acta, **42**, 2219 (1959). ^{b} M. Gorodetsky, A. Yogev, and Y. Mazur, J. Org. Chem., **31**, 699 (1966). ^{c} A. J. Birch, A. R. Murray, and H. Smith, J. Chem. Soc., 1945 (1951).

A different type of behavior was observed for the 3-cyclohexenone systems **86**, studied by Chambers and Marples.[51,52] Both **86a** and **86b** underwent epimerization at one α-carbon upon irradiation in 10% acetone in hexane. Partial quenching of this reaction by naphthalene indicated the involvement of a triplet state. Direct irradiation of **86a** in benzene gave the vinylcyclobutane derivative **87**, the result of a 1,3-shift, and further irradiation of this compound gave decarbonylation (**88**) just as in Williams' study of **80i**.[52] However, **86b** gave epimerization to form **89b**, followed by fragmentation to form **90** and ketene.[52]
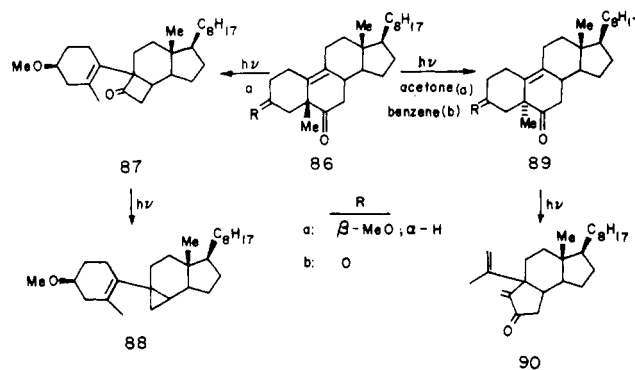
The 3-cyclohexenones resemble the bridged analogs discussed earlier in that the vinylcyclobutanones are formed irreversibly from the 3-cyclohexenones, and the vinylcyclobutanones undergo further reactions such as decarbonylation or ketene loss. A possible explanation is that all these reactions involve α-cleavage, and the resulting diradicals undergo the following processes with decreasing facility: vinylcyclobutanone formation > decarbonylation, ketene formation > 3-cyclohexenone formation. Alternatively, the mode of formation of the diradical may influence its fate, if the diradical is not a thermally equilibrated species.[22]

The ultraviolet spectra of several of the 3-cyclohexenones are given in Table XI. These compounds show neither the bathochromic shift nor the enhanced $n\pi^*$ extinction coefficients observed in most other β,γ-unsaturated ketones.

3. 3-Cycloheptenones and Alkenylcyclopentanones

The bicyclo[3.2.0]hept-6-en-2-ones discussed in section II.A are formally both 3-cycloheptenones and 2-alkenylcyclopentanones, and the "degenerate" 1,3-shifts of these systems may be considered formal interconversions of these two types of molecules. Similarly, the interconversions of 2-norbornenones and bicyclo[3.2.0]hept-2-en-7-ones (section II.C) are formally interconversions of 3-cycloheptenones to 2-alkenylcyclopentanones. The monocyclic derivatives behave analogously.

TABLE XII. Ultraviolet Spectra of 3-Cycloheptenones and 2-Alkenylcyclopentanones

Compd	λ_{max}, nm (ϵ)	Solvent	Ref
	3-Cycloheptenones		
91a	282(41)	MeOH	53
91b	208(1000), 290(27)	C_8H_{18}	53
91c	292(252)	EtOH	45
94b	286(251)	MeOH	54
97	292(220)	MeOH	57
98	sh285(400), 292(460), sh307(410)	MeOH	57
2-Protoadamantenone	296(230)	EtOH	58
	2-Alkenylcyclopentanones		
92a	295(80), 310(90), 325(70), 335(25)	C_8H_{18}	53
93	303(68)	EtOH	45
99	290(110)	MeOH	57

Paquette reported 1,3-shifts of the 3-cycloheptenones **91a** and **91b** upon direct irradiation.[53] Photolysis of **91a** gave a photostationary state of **91a** and **92a** in a ratio of 1:4.[53] The
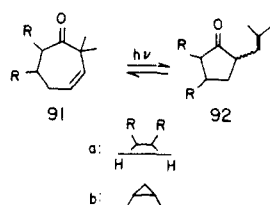
reaction was not quenched by piperylene, and attempted acetone or benzophenonone sensitization led only to slow formation of polymer. These 1,3-shifts were suggested to involve α-cleavage from a singlet excited state.[53]

Williams and Sarkisian studied **91c**, the homoanalog of the fused 3-cyclohexenones studied earlier.[45] While the latter intersystem crosses to a triplet state before a 1,3-shift occurs, **91c** undergoes a 1,3-shift upon direct irradiation. The reaction is reversible, and a photostationary state of 2:3 between **91c** and **93** is formed.[45] The reaction was not sensitized or

quenched, leading to the proposal that an α-cleavage from a singlet excited state was involved and that this was fast only if the ketone α bond and the alkene π bond overlapped effectively.[45] However, the work of Engel et al.[47] in the 3-cyclohexenone series suggests that radical stability, as well as ground-state geometry, plays a role in determination of the facility of α-cleavage.

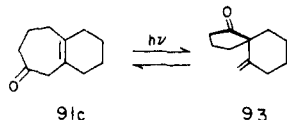Fischer and Zeeh reported that the homosteroids **94a** and **94b** undergo 1,3-shifts upon direct photolysis,[54] and Schaffer reported similar results with **94c**.[55] Seeman and Ziffer[56] recently reinvestigated the photochemistry of **94a** and reversed the assignments of the stereochemistries of **95a** made by Fischer and Zeeh. The major product from **94a** is β-vinyl-**95a**, the compound with $R_1(H)$ and the vinyl group cis, and the minor photoproduct is α-vinyl **95a**. The latter can be photoisomerized to the former, whereas β-vinyl-**95a** is photostable.

Acetone-sensitized irradiation of β-vinyl-**95a** gave the 1,2-shift product **96a**, with the cyclopropane trans to $R_1(H)$, while α-vinyl-**95a** gave **96a** with the cis cyclopropane upon acetone-sensitized photolysis.[56] These reactions do not occur upon direct irradiation; that is, neither **95a** nor **95b** intersystem crosses. The stereospecificity of the 1,2-shift can be interpreted in two ways: either the reaction is a concerted $[_{\pi}2_s + _{\sigma}2_s]$ reaction, or a stepwise mechanism involving initial
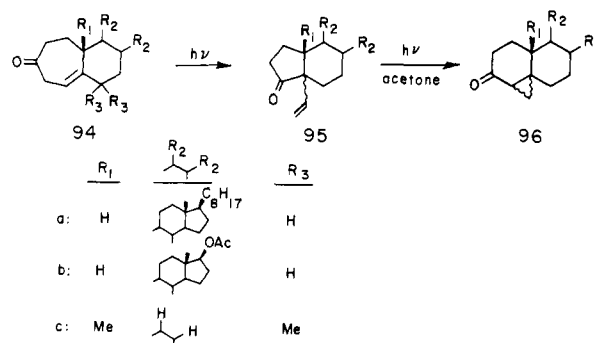
vinyl-carbonyl bridging occurs, involving only the rotamers having the vinyl group away from the steroid nucleus (toward the carbonyl oxygen)[56] (see section II.R).

A series of 1,3-shifts of highly disguised 3-cycloheptenones and 2-vinylcyclopentanones was discovered by Scheffer and Wostradowski.[57] Direct irradiation of **97** (the cycloheptenone moiety is in boldface) gives **98**, which is an alkenylcyclopentanone with respect to the first carbonyl, and a 3-cycloheptenone with respect to the second. Compound **98** undergoes a photoreversible 1,3-shift to give the alkenylcyclopentanone **99**. A photostationary state of **98:99** (1:1.9) was formed. None of the reactions was quenched by piperylene, and attempted sensitization failed or gave polymer.[57]
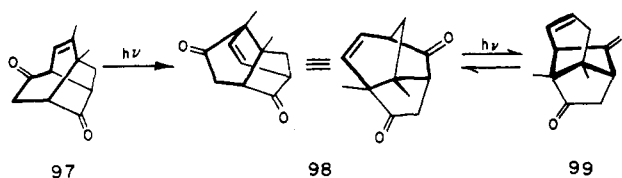
Murray and Babiak recently reported the photochemistry of 2-protoadamantenone (R = H), shown below, and its methyl derivative (R = Me).[58] Direct photolysis of the methyl compound gave a 1,3-shift, resulting in a 1:1 photostationary state. Acetone-sensitized photolysis of 2-protoadamantenone or either methyl isomer gave the corresponding 1,2-shift product.[58]

The available ultraviolet spectra of the compounds discussed in this section are given in Table XII. All of these compounds have λ_{max} at about 290 nm, and the extinction coefficients are about ten times greater for the compounds with alkene tetrasubstitution than for those with disubstituted alkene moieties.

4. 3-Cyclooctenones and 2-Alkenylcyclohexanones

Three of the systems discussed earlier are disguised compounds of this type. Thus, the bicyclo[4.2.0]oct-7-en-2-one discussed in section II.B is both a cyclooctenone and an alkenylcyclohexenone, and the 1,3-shifts of this compound can be considered photochemical interconversions of compounds of that type. Bicyclo[2.2.2]octenones are bridged alkenylcyclohexanones, and their 1,3-shift products are bridged cyclooctenones. These species were discussed in section II.D. Finally, the interconversion of **98** and **99** is formally an interconversion of a cyclooctenone and an alkenylcyclohexanone.

Monocyclic 3-cyclooctenones undergo both 1,3-shifts and form products indicative of intramolecular disproportionation of a diradical resulting from α-cleavage. 3-Cyclooctenone (**100a**) gives mainly a 1,3-shift product, **101a**, and the dienal **102a**.[59,60] The reaction reaches a pseudo-photostationary state of **100a** and **101a** and cannot be sensitized or quenched.[59] A common α-cleaved diradical intermediate in

	X	Y
a	CH₂	-(CH₂)₂CHO
b	O	-OCH₃
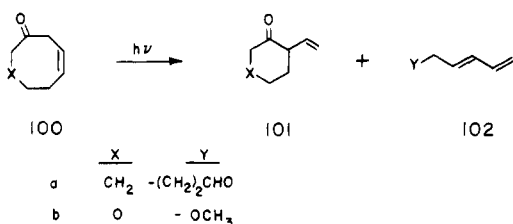
formation of both products was suggested.[60] The oxacyclooctenone **100b** behaves similarly, except that decarbonylation (**102b**) rather than intramolecular hydrogen abstraction competes with the 1,3-shift.[59]

Another type of reaction is observed with 2-alkenylcyclohexanones, namely, the formation of cyclobutanols **105** upon direct irradiation of substituted isopulegones **103**.[61-63] Isopulegone **103a** gives two stereoisomeric cyclobutanols **105a** upon direct irradiation,[61] while both the trans- and cis-acetoxyisopulegones **103b** and **103c** give two cyclobutanols on direct irradiation.[62] The cis-methylisopulegone **103d** behaves in the same fashion.[63] In each case abstraction of the allylic γ hydrogen by an nπ* triplet in a conformation with an equatorial isopropenyl substituent is probable.[63]

	R
a	⋯H
b	—OAc
c	⋯OAc
d	⋯Me
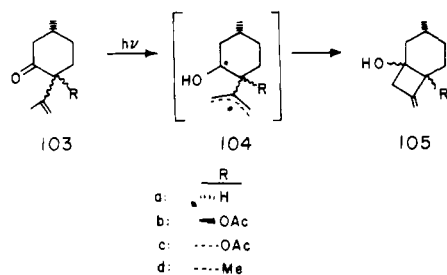
### 5. Cyclononenones and Alkenylcycloheptanones

Although 3-cyclononenes have not been studied, the ethynylcycloheptanone **106** undergoes a photochemical 1,3-shift to give the trappable allene **107** and the aldehyde **108**.[64] No sensitization or quenching was observed, and a common biradical intermediate for formation of **106** and **107** was sug-

	X	R
a	CH	H
b	N	Me
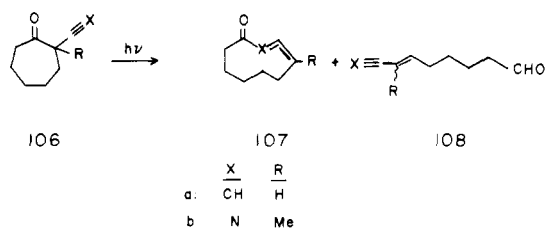
gested.[64] Similar results have been reported with the 2-cyano-2-methylcycloheptanone (**106b**), and 2-cyano-2-methylcyclohexanone.[65] Irradiation of **106b** in methanol gives a mixture of the Z and E aldehydes **108b**, along with a small amount of the result of methanol addition to the cyclic ketenimine **107b**.[65]

6. 3-Cyclodecenones and Alkenylcyclooctanones and Larger 3-Cycloalkenones

Whereas the 3-cyclooctenenes undergo both 1,3-shifts and diradical disproportionation, and both are suggested to involve the same diradical intermediate, 3-cyclodecenone (**109**) undergoes only a photoreversible 1,3-shift on direct irradiation.[66] Carlson and Bateman suggested that a conformationally rigid diradical must rapidly reclose, since an equilibrated diradical would be expected to undergo other radical reactions without reclosure.[66]
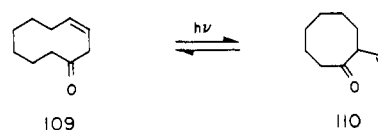
Four reports about the photochemistry of cyclodeca-3,8-diene-1,6-dione and derivatives have appeared.[67-70] Shani reported that the cis,cis compound **111a** gave both the cis, trans isomer **112a** and the syn-fused cyclobutane corresponding to the anti **113a** on direct irradiation in benzene.[67] However, both Scheffer[68] and Conrow[69] found that the cis, trans isomer **112a** was the only primary product of photolysis of **111a** and that **112a** underwent a photochemical intramolecular cycloaddition to form the anti cyclobutanone **113a**.

	R	R	R'	R'
a:	=O		=O	
b:	=O		OMe	OMe
c:	OMe	OMe	OMe	OMe
d:	H	H	H	H
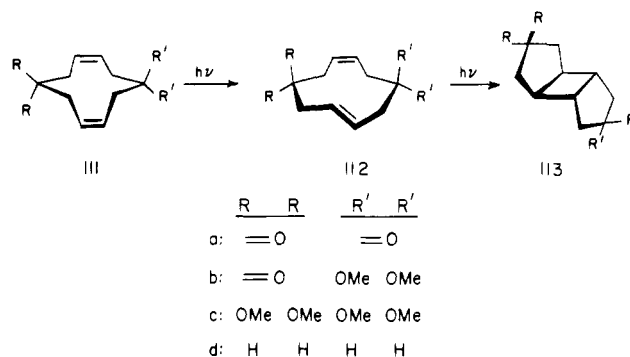
The behavior of **111a** is unusual in that no products of α-cleavage and/or 1,3-shift are observed. The preferred conformation of **111a** is that shown in the drawing.[71] If α-cleavage occurs, several severe nonbonding interactions would ensue upon rebonding of the acyl radical to the γ carbon. Apparently, intersystem crossing to a triplet state, which cis, trans isomerizes to form **112a**, occurs. The conversion of **112a** to **113a** is most likely also a triplet reaction involving a diradical intermediate,[68] since irradiation of **111a** in acetone gives **113a**.[69]

The related compounds **111b-d** were also studied by Shani,[70] who found that the β,γ-unsaturated ketone **111b** gives **112b** and **113b** upon photolysis in benzene, while the dienes **111c** and **111d** were converted into the cyclobutanes **113c** and **113d** upon acetone-sensitized photolysis.[70]

In a reinvestigation of the photoisomerizations of 2-cyclododecenone, Marchesini et al.[72] found that trans-3-cyclododecenone (**114**), the major product of photochemical deconjugation of the conjugated isomer, was converted into a photostationary state (84:16) of the trans (**114**) and cis (**115**) isomers upon irradiation in cyclohexane. Once again, transannular strain in the possible 1,3-shift product may prevent any

TABLE XIII. Ultraviolet Spectra of 3-Cycloalkenones ($>C_8$) and 2-Alkenylcycloalkanones

Compd	λ_{max}, nm (ϵ)	Solvent	Ref
100a	292(47)	C_6H_{14}	60
	290(60)	MeOH	60
109[a]	287(67)	EtOH	66
114	289(59)	95% EtOH	72
115	294(562)	95% EtOH	72
101a	296(20)	C_6H_{14}	60
103b	292(166), 297(166)	C_7H_{16}	62
	sh260(186), 287(174)	EtOH	62
103c	240(288), 294(174)	C_7H_{16}	62
	252(275), sh290(95)	EtOH	62
103d	298(42)		63
106	290(64), sh296(55), sh308(37)		64
110	293(81)	EtOH	66
116	296(292)	EtOH	73

[a] Contaminated with trans-4-cyclodecenone.
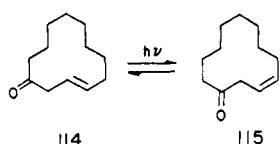
observable singlet reaction, so that intersystem crossing occurs, leading to cis,trans isomerization. However, no experiments have been carried out to prove the triplet nature of this reaction. Finally, the 2-allenylcyclododecanone derivative 116 undergoes a 1,3-shift upon direct irradiation.[73]
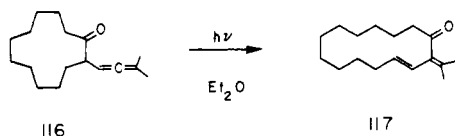
Ultraviolet spectra of some of the compounds discussed in this section are given in Table XIII. In general, all these compounds absorb at about 290 nm, and the $n\pi^*$ enhancements for these compounds are considerably lower than those for the rigid polycyclic systems discussed earlier.

G. 3-Alkylidenecycloalkanones

In this series, the 1,3-shifts are degenerate in the absence of asymmetrically located substituents.

1. 3-Alkylidenecyclobutanones

The photochemistry of the parent 3-methylenecyclobutanone (118a) was elucidated in a series of elegant investigations by Dowd et al.[74-76] The photolysis of 118a in perfluorinated solvents at $-196°$ gave CO and trimethylenemethane (120) which was detected by esr spectroscopy.[74] Direct photolysis of 118 in butadiene solvent gave the oxetane 121,

along with trimethylenemethane trapping products. The tetradeuterated compound 118b gave the deuterium scrambled compound 118c.[75] Thus, 3-methylenecyclobutanone undergoes α-cleavage, and the resulting diradical can reclose to give a 1,3-shift product or can lose CO.[75,76] In addition, oxetane formation can occur in the presence of a diene.
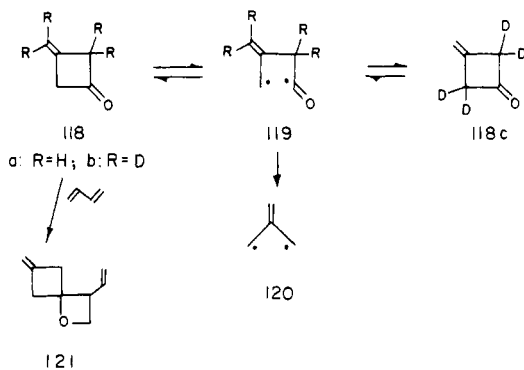
Several studies of highly substituted 3-methylenecyclobutanones have been reported. Hostettler found that irradiation of $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-3-dicyanomethylenecyclobutanone decarbonylates upon irradiation in benzene, while an acetal, the result of trapping of a cyclic oxacarbene, is also formed in methanol solution.[77] Several other reactions of this type have been found.[22,77,78]

2. 3-Alkylidenecyclopentanones

An example of a 1,3-shift in a bridged 3-isopropylidenecyclopentanone, 50, was cited earlier. No other examples of this type have been studied.

3. 3-Alkylidenecyclohexanones

Paquette and Meehan[79] reported the first examples of photochemistry of these extensively studied species. Direct irradiation of 122a, 122c, and 122e gave photostationary states with the 1,3-shift isomers 123a, 123c, and 123e in ratios of 10:1, 4:1, and 6:1, respectively.[79] Northington found that a photostationary state of 3.4:1 between 122c and 123c was obtained on irradiation at 254 nm, and a quantum yield of 0.05 was observed for the conversion of 122c to 123c.[80]
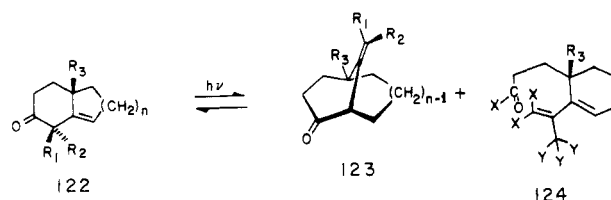
	R_1	R_2	R_3	X	Y
a:		Me	Me	Me	H	H
b:		Me	Me-d_3	Me	H	D
c:		Me	Me	H	H	H
d:		Me-d_3	Me	H	H	D
e:		Me	Me	H		

A thorough study of deuterated analogs of these compounds by Nakanishi et al.[48] revealed that both 123a and aldehyde 124a were formed on irradiation of 122a in a variety of solvents. The trideuteromethylated compound, consisting mainly of 122b (9:1 with the CD_3 epimer), gave a stereospecific 1,3-shift to form 123b (9:1 with the CD_3 epimer) and 124b (9:1 with compound where X = D and Y = H). Thus, the hydrogen abstraction occurs only from one of the methyl groups. Irradiation of 123a gave both 122a and 124a. Similarly, irradiation of 122d (7:3 with the CD_3 epimer) in several solvents gave a stereospecific 1,3-shift to form 123d (7:3 with the CD_3 epimer), but a nonstereospecific hydrogen transfer to give a 1:1 mixture of 124d and the compound with X = D and Y = H. Irradiation of 123c gave both 122c and 124c. None of these reactions was sensitized by acetophenone or quenched by trans-piperylene.[48]

Nakanishi et al. suggested that these reactions proceeded by α-cleavage from an $n\pi^*$ singlet state to form a solvated intimate radical pair 125 in a chair-like conformation. Recombination to give the 1,3-shift product occurs within the solvent cage, without rotation about the partial double bond of the allylic radical, and thus the 1,3-shift is stereospecific. Aldehyde formation results from free, not intimate, biradical intermediates. It was further proposed that the angular methyl group

125
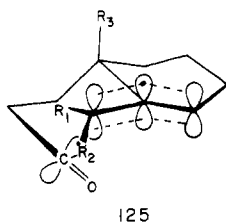
(R_3 = Me) prevented free rotation of the allyl radical, so that only hydrogen abstraction from the "inner" methyl occurs (R_1), while free rotation occurs when R_3 = H.[48]

Different behavior has been reported of a number of steroidal 3-alkylidenecyclohexanones of this type. For example, cholest-5-en-3-one, which lacks α,α-disubstitution, is quite photostable,[48] while **126** undergoes protonation of the double bond, followed by deprotonation to give **126**-d and **127**.[81] A

126   126-d   127
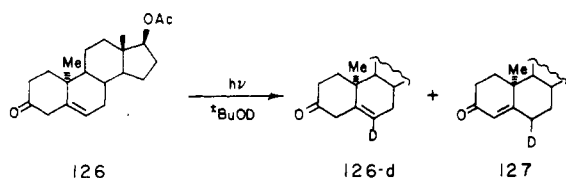
charge-transfer excited singlet state or twisted $\pi\pi^*$ triplet was proposed by Kuwata and Schaffner as possible excited state species which undergo protonation.[81] Nakanishi suggested that the failure of species of the latter type to undergo 1,3-shifts resulted from insufficient stabilization of the incipient diradical unless α-substituents were present.[48]

In support of this, the analogous 4,4-dimethyl steroids do give products indicating that initial α-cleavage occurs, but no 1,3-shift products were obtained. Thus, **128a** gives oxetane **130** on irradiation in benzene, while **128b** gives a different oxetane, **131**.[82] Both of these could arise from the dienylal-

	R_1	R_2
a:	Me	CD_3
b:	CD_3	Me

132

128   129   130

	R
a:	H
b:	Me

131
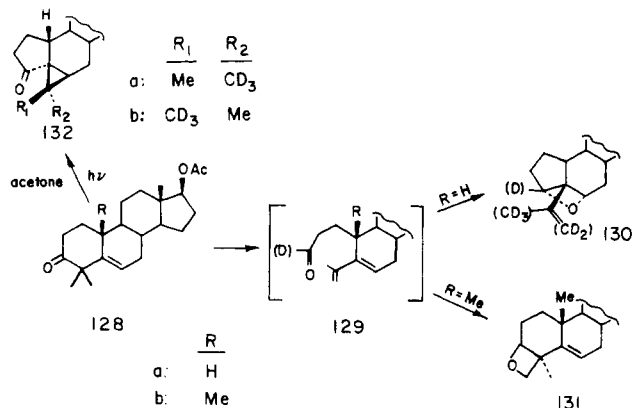
dehydes **129**. The absence of 1,3-shift products is perplexing unless irradiation was carried out for a sufficiently long period of time that **128, 129** and a 1,3-shift product were all converted irreversibly to the oxetanes. Acetone-sensitized photolysis of **128** gave the 1,2-shift product **132**.[83] Nakanishi and co-workers found that **132** had a β-cyclopropyl, and that acetone-sensitized irradiation of a 66:44 mixture of α-4-trideuteriomethyl-**128a** and β-4-trideuteriomethyl-**128a** gave a 53:47 mixture of **132a** and **132b**. This r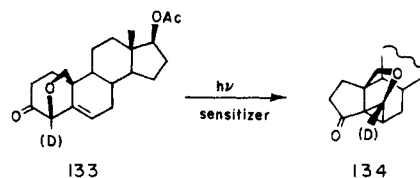esult requires either an oxa-di-π-methane rearrangement with a biradical intermediate capable of scrambling the methyls, or else formation of such a biradical from further photoreactions of the cyclopropyl ketones **132a,b**.[49] If the former obtains, this result is profoundly significant. However, stereospecificity observed in several other 1,2-shifts suggests that the lack of stereospecificity here has the latter trivial origin.[454]

Kojima et al. also reported a sensitized 1,2-shift in the related compound **133**.[83] This reaction was sensitized by keton-

ic sensitizers of E_T = 69–82 kcal/mol and benzene (E_T = 85 kcal/mol),did not occur in alcohols or dioxane in the absence of sensitizer, and was quenched by piperylene ($E_T \sim$ 57 kcal/mol) and naphthalene (E_T = 60 kcal/mol).[83] This compound is unusual in that no 1,3-shift occurs and no intersystem crossing occurs. This suggests that α-cleavage occurs, but rebonding in a 1,3-fashion does not occur.

Nakanishi et al. have reported detailed studies of the substituted cholest-4-en-7-ones (**135**).[84–86] In contrast to the cholest-5-en-3-one series cited earlier, both the α,α-dimethyl compound **135a** and the unmethylated compound **135b** undergo 1,3-shifts to form photostationary states with **136a** and **136b** of 1:7 and 1:1, respectively.[48] The absence of aldehydes in these reactions was suggested to be due to the fact that the intermediate diradical cannot achieve the conformation required to abstract a hydrogen from a direction perpendicular to the incipient allyl radical.

133   134

135   136
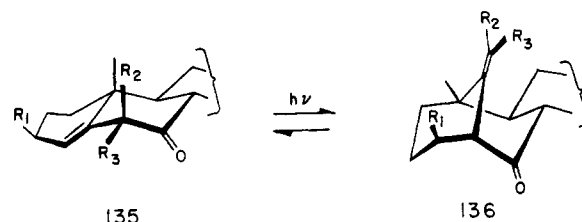
	R_1	R_2	R_3
a:	H	Me	Me
b:	H	H	H
c:	OAc	H	H
d:	OMe	H	H

When any one of the ketones **135b–d**, deuterated predominantly at R_2, was irradiated, a photostationary state was obtained without deuterium scrambling, indicating a lack of rotation of the intermediate allyl radical.

The use of circular dichroism to follow the 1,3-shifts was reported by Nakanishi and coworkers.[86] Using this technique, they found that the quantum yield of conversion of **135b** to **136b** was 0.1 at 290 nm, while that for the reverse reaction was 0.3 at 290 nm. Neither *trans*-piperylene nor acetophenone had any affect on these quantum yields.[86]

Finally, Hayashi et al. found that irradiation of cholest-4-en-7-one (**135b**) in the presence of the conjugated isomer, cholest-5-en-7-one, gave oxetanes resulting from addition of the carbonyl of **135b** to the conjugated double bond of cholest-5-en-7-one.[85]

139   137   138

	R
a:	H
b:	Me
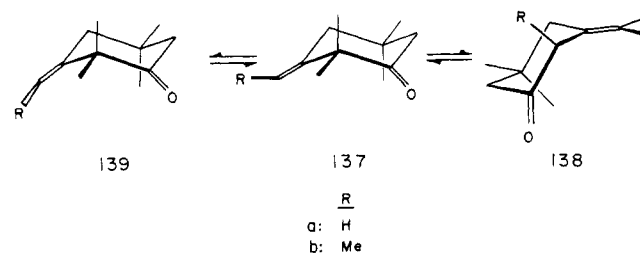
Hancock and Grider studied 3-methylenecyclohexanones in which the methylene groups can undergo free rotation in the excited state. Direct irradiation of **137a** gave a 1:1 photostationary state of the 1,3-shift isomers **137a** and **138a**.[87] The

TABLE XIV. Ultraviolet Spectra of 3-Alkylidenecycloalkanones

Compound	λ_{max}, nm (ϵ)	Solvent	Ref
118	215(1550), 266(12), 275(19), 293(22) 308(15), 320(8)	C_6H_{12}	74
122a	228(35), 296sh(35), 305sh(30)	C_8H_{18}	79
122c	289(80), 297(85), 306(75), 317(40)	C_8H_{18}	79
122e	289(90), 298(95), 308(85), 319(45)	C_8H_{18}	79
123a	286(145), sh300(125)	C_8H_{18}	79
123c	293(130), 302(130), 311sh(100)	C_8H_{18}	79
123e	288(360), 296(420), 305(390), 317(225)	C_8H_{18}	79
Cholest-5-en-3-one	296(56)	C_6H_{12}	48
126	222(931), 295(121)	t-BuOH	80
	298(122)	C_6H	80
128a	296(100)	EtOH	83
133	313(260)	EtOH	83
135a	295(105)	EtOH	48
135b	290(240)	EtOH	84
136a	298(58)	EtOH	48
136b	297(48)	EtOH	84
136c	280(304)	EtOH	84
137a	298(72)	C_6H_{12}	90
137b	298(104)	C_6H_{12}	90
138a	298(118)	C_6H_{12}	90
138b	299(113)	C_6H_{12}	90
139b	298(54)	C_6H_{12}	90

conversion of **137a** to **138a** had a quantum yield of 0.13. No quenching or sensitization of the 1,3-shift could be achieved, and the unreactivity of the triplet state was attributed to deactivation of the triplet excited state by the "free rotor" effect which has been used as a rationalization of the lack of reactivity of conformationally nonrigid di-π-methane systems.[88] This explanation was given credence by the observation that **137b** and **139b** were readily interconverted upon sensitized irradiations using sensitizers with E_T = 65–74 kcal/mol.[89] Direct irradiation of the mixture of **137b** and **139b** gave **138b** with a quantum yield of 0.20.[89] The drawings shown here indicate the preferred conformations of these species, although for the 2,2,5,5-tetramethyl-3-methylenecyclohexanone the barrier to inversion is only 5.9 kcal/mol.[91] Owing to "allylic strain",[92] the methyl group of **138b** is probably axial, and the stereospecific conversion of **138b** to **137b** (Φ = 0.30) observed by Hancock and Grider[90] can be construed as a result of rapid α-cleavage of **138b** from a conformation preferred in the ground state. Alternatively, a concerted 1,3-shift is also compatible with this observation.

The ultraviolet spectra of the alkylidenecycloalkanones are given in Table XIV. In most cases, the nπ* enhancements are modest. Methylenecyclobutanone, which must be nearly planar, has a weak nπ* transition, while the methylenecyclohexanones all absorb at about 297 nm with extinction coefficients normally in the range of 50–200.

H. Acyclic and Related β,γ-Unsaturated Ketones

1. Acyclic Ketones

Studies of acyclic β,γ-unsaturated ketones preceded much of the work reviewed so far. Several simple derivatives of pent-4-en-2-one undergo α-cleavage and, if a single substituent is present on the β carbon (C-6), cis,trans isomerization. Irradiation of pent-4-en-2-one (trans-**140a**) in the gas phase at 313 nm results in α-cleavage with formation of CO (Φ = 0.60) and radical coupling products such as biacetyl, ethane, and 1,5-hexadiene.[93] The β-methyl derivative, trans-hex-4-en-2-one (trans-**140b**), undergoes rapid isomerization to the cis isomer (cis-**140b**) upon direct irradiation.[94] The α-cleavage and formation of a complex radical coupling mixture occurs more slowly. The α,α-dimethylated compound **140c** disappears with a quantum yield of 0.60 upon irradiation in
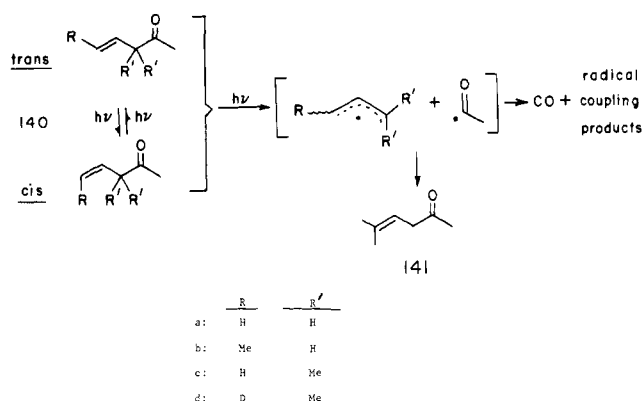
benzene at 313 nm to give the 1,3-shift product and **141** (Φ = 0.15), biacetyl, and products of coupling of the dimethylallyl radical.[95] Presumably, the products are all formed after initial α-cleavage. Irradiation in acetone gives no detectable reaction, but irradiation of the deuterated analog, trans-**140d**, in acetone gives cis,trans isomerization. Since **140c** does not quench the type II reaction of butyrophenone ($E_T \approx$ 75 kcal/mol), the triplet state responsible for the cis,trans isomerization must lie around 78 kcal/mol, the triplet energy of acetone.[95]

One of the first examples of the oxa-di-π-methane rear-

rangement was observed by Dauben and coworkers, who coined the name for this reaction.[96] Sensitized photolysis of **142a** gave **143**, while direct photolysis gave the 1,3-shift product **144a**, which, upon further irradiation, formed decarbonylated products resulting from recombination of isopropyl and phenyldimethylallyl radicals. The diradical shown below **143** was suggested as an intermediate in the sensitized reaction.[96] Conia reported a 1,3-shift upon photolysis of the related ketone **142b**.[97] Pratt reported that **142c** gives a rapid 1,3-shift on direct photolysis, but that sensitized irradiation gives a complex mixture containing no oxa-di-π-methane product.[98]
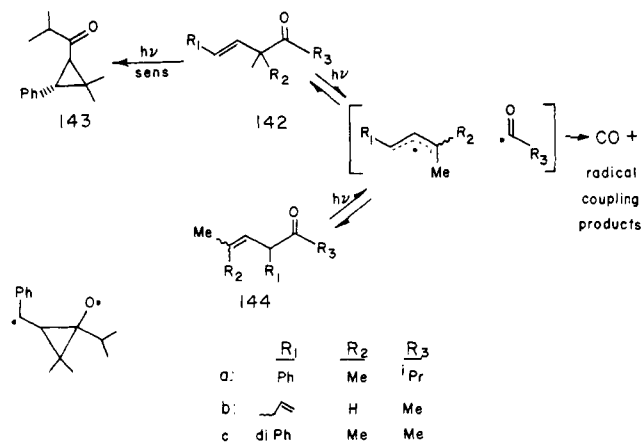
An additional reaction is observed with cyclic β,γ-unsaturated ketones with a β-alkyl substituent. These species undergo type II hydrogen abstraction reactions with formation of cyclobutanols in addition to α-cleavage. Yang and Thap reported that **145a** disappears with high efficiency ($\Phi^{313nm} = 0.33$) in pentane to give cyclobutanol **147a** ($\Phi = 0.22$) as well as a number of compounds expected from α-cleavage of **145a** followed by radical recombinations, such as 2,5-dimethyl-2,5-hexadiene ($\Phi = 0.05$).[99] Piperylene had little effect on the quantum yields of product formation.[99]
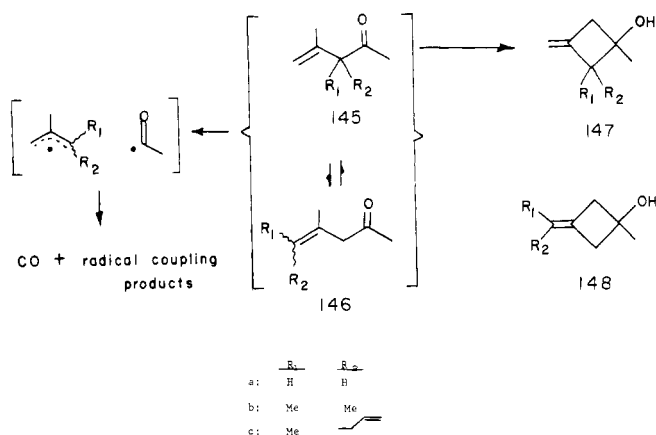
Kiefer and Carlson found that photolysis of **145b** gave the 1,3-shift product **146b** (32%) and cyclobutanols **147b** (55%) and **148b** (8%), along with small amounts of products resulting from α-cleavage–recombination reactions.[100] Photolysis of **145b** in the gas phase resulted in formation of α-cleavage products, but none of the 1,3-shift product, leading to the suggestion that the 1,3-shift in solution involves α-cleavage and cage recombination of a radical pair.[100] The analog **145c** was reported to give only cyclobutanol **147c** upon direct irradiation.[97]

Not all β-alkyl compounds undergo the type II reaction. Engel and Schexnayder have found that **149** gives oxetane **150** upon direct irradiation along with 1,3-shift product and traces of cyclobutanols.[101] This ketone was specifically studied to test Engel's hypothesis that β,γ-unsaturated ketones with electron-rich alkene double bonds would form oxetanes rather than undergo α-cleavage or type II reactions.[101]
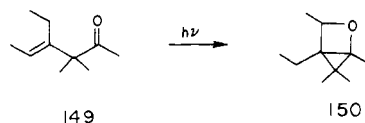
Engel and Schexnayder recently reported a very thorough study of a bis(β,γ-unsaturated) ketone, **151**.[102] Photolysis of **151** gave carbon monoxide ($\Phi = 0.30$) and the products of coupling of two 3-methylbutenyl radicals. The ratio of these products was essentially the same as that found on photolysis of the corresponding azo compound.[103] When run at low conversion or at low temperature in a glass, the 1,3-shift product **152** could also be isolated.[102] The authors suggested that the
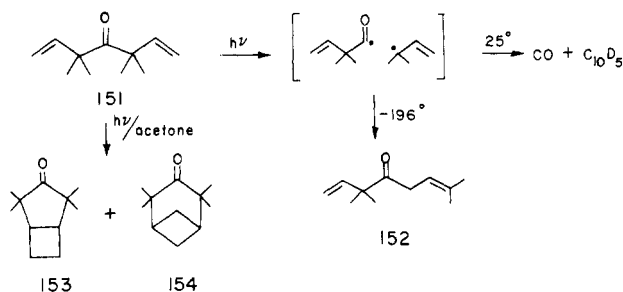
recombination occurs with lower activation energy than the decarbonylation. No quenching of decarbonylation by piperylene or cyclohexadiene was observed. Acetone-sensitized photolysis of **151** gave the cyclobutanes **153** and **154** with a quantum yield of 0.19 for **151** disappearance. The ketone **151** did not quench the type II reaction of butyrophenone ($E_T = 75$ kcal/mol), indicating that the triplet state of **151** lies near that of acetone in energy. The bulky α-methyls were assumed to favor a conformation in which intramolecular [2 + 2] cycloadditions would occur.[102]

Engel has made an interesting comparison between the quantum yields for disappearance of ketone (mainly due to decarbonylation) for saturated and β,γ-unsaturated analogs shown in Table XV. Introduction of one or two β,γ-double bonds into the ditertiary ketone (first entry of Table XV) reduces the quantum yield for ketone disappearance, but also renders the excited state unquenchable by 2 M piperylene. These results are compatible with rapid α-cleavage from the $n\pi^*$ singlet state for the unsaturated ketones, and mainly from the triplet for the saturated ketone.

The photochemistry of the related γ,δ-unsaturated ketones are of some interest in connection with the studies reviewed here. Srinivasan studied the photolysis of **155a** at 313 nm in the gas phase.[104] The compound proved to be very stable, undergoing slow conversion to the oxetane **156a** with $\Phi = 0.006$. At shorter wavelengths, products of α-cleavage recombination reactions were also observed.[104] Yang and coworkers found that both **156a** and **157a** were formed by irradiation of **155a** in solution although **157a** could not be isolated.[105] The irradiation of **155b** in pentane solution yielded **156b** and **157b** in a ratio of 2:5.[104] Thus, when the double bond is situated γ,δ to the carbonyl group, there is little tendency for α-cleavage, and reactions characteristic of carbonyl $n\pi^*$ states intervene instead.
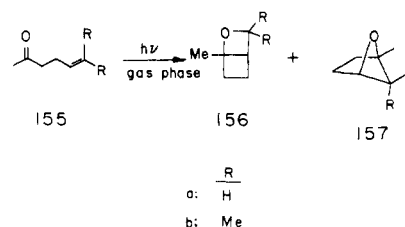
The ultraviolet spectra of the acyclic compounds discussed here are given in Table XVI. In general, $n\pi^*$ enhancement is

TABLE XVI. Ultraviolet Spectra of Acyclic β,γ-Unsaturated Ketones

Compound	λ_{max}, nm (ϵ)	Solvent	Ref
139a	284.5(32)	C_6H_{12}	93
139b	280(79)	MeOH	94
139c	290(78)	C_6H_{14}	a
cis-142a	284(47), 292(89)	EtOH	96
trans-142a	253(14950), 285(292), 293(376)	EtOH	96
144b	289(160), 296(164), 306(145)	C_6H_{12}	97
145a	283(72)		99
3-Acetoxy-4-methylpent-4-en-2-one	241(282), 287(170)	EtOH	62
	235(288), 294(162)	C_7H_{16}	62

a P. S. Engel, private communication.

modest, except in the compounds containing conjugated alkenes.

2. Acetonylcycloalkenes

The photochemistry of these species is as diverse as that of the acyclic species but has been subjected to more systematic scrutiny. Engel and Schexnayder have studied the dimethylacetonylcycloalkenes with cycloalkene ring sizes of 4–8.[95,101] The cyclobutene **158** undergoes both α-cleavage, as shown by the formation of biacetyl, and a 1,3-shift upon direct irradiation. Acetone-sensitized photolyses of **158** or **159** also gives 1,3-shifts, apparently unprecedented occurrences in the photochemistry of β,γ-unsaturated carbonyls. The cyclopentene **159a** undergoes a 1,3-shift upon direct irradiation to give **160a**, but the photoproduct **160a** does not revert to **159a** upon photolysis. The quantum yields measured by Engel and Schexnayder for this and similar reactions discussed in this section are given in Table XVII. Givens and coworkers obtained a 1:1 photostationary state between **159b** and **160b** upon direct irradiation in hexane at 300 nm.[106]
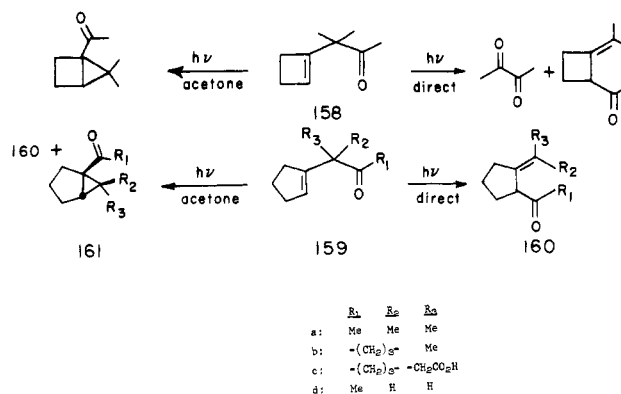
The acetone-sensitized irradiations of both **158** and **159a** are unusual, in that both the 1,2-shift products **161a** and the 1,3-shift product **160a** were formed,[95,101] while Carlson et al. reported that acetone-sensitized photolysis of **159b** or **160b** gave only the 1,2-shift product **161b**.[106] There are spectroscopic differences in **159a** and **159b** which may be relevant and are discussed later.

Givens and coworkers have recently studied the photochemistry of optically active **159c**.[107] Direct irradiation of this compound gives the optically active 1,3-shift product **160c**, and the CD spectrum of this compound indicates that the 1,3-shift is suprafacial. The result is consistent with any of the following possibilities: (1) a concerted reaction, (2) initial C_{CO}–C_γ bonding, followed by α-cleavage, or (3) α-cleavage followed by recombination which is much faster than rotations which would racemize the radical-pair intermediate. Longer irradiation times resulted in racemization of **160c**.[107] This is likely a result of recombinations of external radical pairs formed from α-cleavage and diffusion out of the solvent cage.

The irradiation of (R)-**159c** in acetone gave optically active **161c** with ≥90% optical purity. The CD spectrum indicated the stereochemical relationships shown in Figure 3. The ob-

TABLE XVII. Quantum Yields of Photochemical Reactions of Acetonylcycloalkenes

Compd	Direct irradiation					Acetone-sensitized irradiation		
	$\Phi_{-K}{}^a$	$\Phi_{\alpha\text{-cleavage}}$	$\Phi_{1,3}$	$\Phi_{cyclobutanol}$	$\Phi_{oxetane}$	$\Phi_{-K}{}^a$	$\Phi_{1,3}$	$\Phi_{1,2}$
158	0.58	+	0.28			0.45	0.22	0.09
159a	0.31		0.04	0.02		0.25	0.15	0.03
159d	0.22		0.01	0.06	0.02^b	0.35		0.12
162a	0.24			0.10	0.02	0.009		
164a	0.18			0.03	0.02	0.05		
167a	0.15			0.007	0.05	0.05	(trans probably formed)	

a Ketone disappearance. *b* 1,2-Shift product formed on direct irradiation.
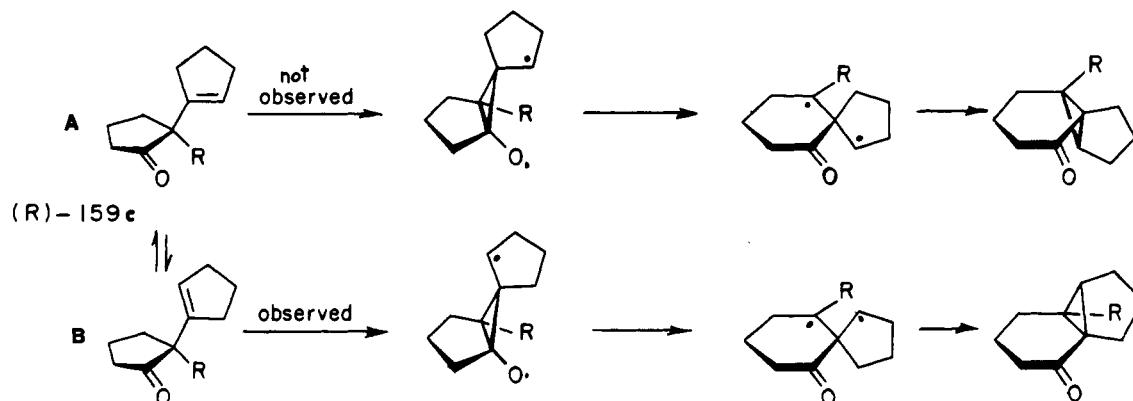
Figure 3. The stereochemistry of the oxa-di-π-methane rearrangement of (R)-**159c**.

served result (bottom path) corresponds to inversion of configuration at the chiral center present in **159c**. Givens and coworkers interpreted this result as evidence for a concerted $[_{\pi}2_a + _{\sigma}2_a]$ pathway.[107] However, the result is also compatible with a stepwise mechanism such as that shown in Figure 3, as long as the initial bond formation occurs only from rotamer B, and not from rotamer A. The result is like that of Seeman and Ziffer reported earlier;[56] that is, bond formation occurs in both cases from the rotamer which appears to be least crowded.

The acetonylcyclopentene **159d**, lacking the α-methyl groups, behaves differently in that direct irradiation gives a 1,3-shift (cyclobutanol) and some of the 1,2-shift product. It appears that this last compound, like the 1,2-shift product from 3-octalone, is formed after intersystem crossing and a subsequent triplet reaction.[101]

The cyclohexenes **162** behave much differently in that the type II cyclobutanols, **163**, are the exclusive products of direct irradiation. Engel and Schexnayder found that **162a** disappears with a quantum yield of 0.24 to form **163a** with a quantum yield of 0.10.[95] The acetone-sensitized irradiation of

162

163

	R₁	R₂	R₃	R₄	R₅
a:	Me	Me	Me	H	H
b:	Me	H	H	H	H
c:	Me	H	H	Me	H
d:	Me	H	H	H	Me
e:	-(CH₂)₄—		H	H	H
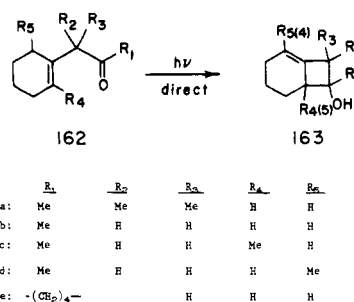
162a results in a very slow disappearance of the starting material ($\Phi = 0.009$) without formation of detectable products. Dalton and Chan reported a similar type II reaction with the unmethylated cyclohexene **162b**.[108] Direct irradiation gave both (Z)- and (E)-cyclobutanols **163b**, with quantum yields of 0.055 and 0.02, respectively. The methyl derivatives **162c** and **162d** gave the same mixture of three isomeric cyclobutanols **163c** and **163d** upon direct irradiation, indicating that the same long-lived 1,4-biradical is formed from either **162c** or **162d**.[108] These reactions were not quenched by piperylene, and acetone-sensitized photolysis gave mainly polymer and only small amounts of cyclobutanols, indicating a singlet excited state for hydrogen abstraction. Cookson and Rogers found a similar result with 2-cyclohexenylcyclohexanone (**162a**). Direct irradiation of a mixture of the α,β- and β,γ-unsaturated ketones **162e** in cyclohexane gave the cyclobutanol **163e**.[109]

Dalton and Chen recently reported the reactions shown below, which involve the formal 1,3-shift isomers of the acetonylcycloalkenes. As with their isomers, no 1,3-shifts are observed upon direct irradiation, but type II reactions occur when the acetyl is axial, and oxetane formation occurs when the acetyl is equatorial.[110]
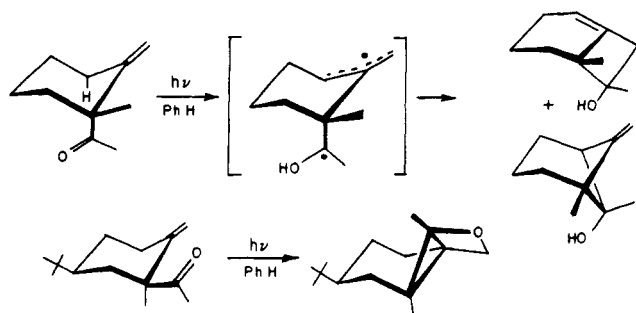
In the seven- and eight-membered ring series, still different results are obtained. Cookson and Rogers reported that **164b** and **167b** were converted into the oxetanes **165b** and **168b**, respectively, upon direct irradiation.[109] This report of oxetane formation, at the time unprecedented, was followed by Engel and Schexnayder's report that **164a** and **167a** give both oxetanes and cyclobutanols upon direct irradiation.[101] Although **164a** and **167a** disappear on acetone-sensitized photolyses, no products have been isolated from these reactions.[101] Engel and Schexnayder have obtained indirect evidence for the formation of the trans cycloalkene upon sensitized irradiation of **167a**.

164   165   166

	R₁	R₂	R₃
a:	Me	Me	Me
b:	-(CH₂)₅-		H

167   168   169

	R₁	R₂	R₃
a:	Me	Me	Me
b:	-(CH₂)₆-		H
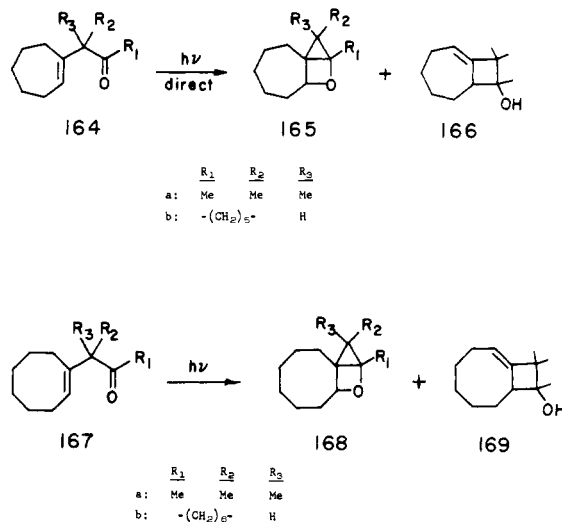
Engel and Schexnayder have provided a rationale for the variation in behavior of β,γ-unsaturated ketone singlets as the alkene substitution is changed. They suggested that when the double bond is sufficiently electron-rich (e.g., **149, 164a, 167a**), then the $n\pi^*$ excited state has considerable charge-transfer ($\pi_{CC} \rightarrow \pi^*_{CO}$) character, and this excited state collapses to oxetane or back to ground state. Thus, an increase in ring size, which decreases the alkene ionization potential, results in faster singlet deactivation or, when the ring is sufficiently electron releasing, oxetane formation. By contrast, in the absence of a very electron-rich alkene moiety, normal $n\pi^*$ reactions such as γ-hydrogen abstraction or α-cleavage occur.[101] This hypothesis is discussed in more detail in the spectroscopic and theory section of this review.

3. Acylcycloalkenes

The involvement of acylcyclopropenes and related species in the photoisomerizations of heterocycles has been shown in a number of cases. Two studies have resulted in the isolation of these types of species and the elucidation of their photochemistries. Van Tamelen and Whitesides found that **170** undergoes photoisomerization to **171**, the photochemical precursor of **170**, as well as to the isomeric furan **172** and the allenyl ketone **173**.[111] The mechanisms proposed for these reactions involve cleavage of one or the other cyclopropene single bonds (β-cleavage) and collapse of the resulting diradicals to products. Thus, these reactions appear to follow pathways characteristic of cyclopropyl ketones rather than β,γ-unsaturated ketones.

171   170   172   173
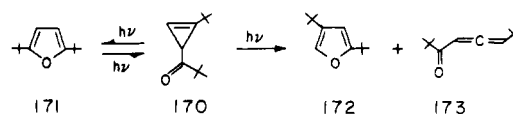
A classic example of a 1,3-shift on direct photolysis and 1,2-shift on sensitized photolysis was reported by Baggiolini,

TABLE XVIII. Ultraviolet Spectra of Acetonyl- and Acylcycloalkenes

Compound	λ_{max}, nm (ϵ)	Solvent	Ref
158	288(106), 296(106)	C_6H_{14}	101
159a	300(118)	C_6H_{14}	101
159b	258(342), 287(105), 302(129), 311(120), 323(63)	C_8H_{18}	107
159c	313(120)	C_8H_{18}	a
159d	290(75)	C_6H_{14}	101
162a	299(199)	C_6H_{14}	101
164a	298(106)	C_6H_{14}	101
167a	300(119)	C_6H_{14}	101
3-Methyl-3-acetyl-cyclopropene	200(1450), 218(1500), 290(120)	C_6H_{14}	b
1-Methyl-3-acetyl-cyclopropene	206(3000), 288(82)	C_6H_{14}	b
174a	300(151)	C_8H_{18}	113
174e	300(101)	C_8H_{18}	114
	295(102)	EtOH	114

^{a} R. S. Givens, private communication. ^{b} H. Monti and M. Bertrand, *Tetrahedron Lett.*, 1235 (1969).

Schaffner, and Jeger.[113] Irradiation of optically active (+)-**174a** gave racemization and products resulting from α-cleavage followed by recombination, such as **176**. The 1,3-shift racemization was 32% of the photochemical reaction of **174a**. Photolysis of either **174b** or **174c** gave scrambling of deuteriomethyls to form **175b** and **175c**, respectively. The scrambling occurred at the same rate as racemization of **174a**.

Photolysis of a mixture of the two trideuteriomethyl compounds gave no d_6 material, indicating that the 1,3-shift is wholly intramolecular. Thus, the reaction is either concerted or involves cage recombination where the acetyl radical recombines on the same side of the cyclopentenyl radical as that from which it is α-cleaved.[113] Alternatively, α-cleavage followed by random cage-recombination would be compatible with these results.
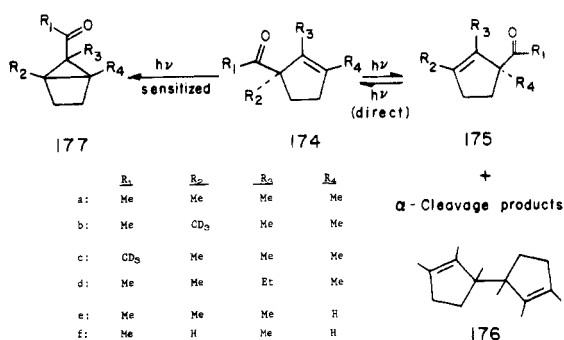
Acetone-sensitized irradiation of **174a** gave the 1,2-shift product **177a**.[113] Recently, Schaffner and Gonzenbach have studied the sensitized photolyses of **174a**, **174d**, **174e**, and **174f**.[114] The formation of **177d** and **177f** from the respective ketones proves the oxa-di-π-methane nature of the rearrangement.[114,115] The ratios of stereoisomeric housanes **177** formed in the sensitized reactions are of great interest, since these ratios are different from those obtained upon thermal equilibration, which presumably involves cleavage of the internal cyclopropyl bond and formation of a 1,3-diradical. The endo-acetyl and exo-acetyl products were obtained in ratios of 5:1, 7:1, and 3:1 from **174a**, **174e**, and **174f**, respectively, while the corresponding thermal equilibrium ratios are 1:26, 1:3, and 1:5.7, respectively.[114] Thus, the distinct preference for the endo-acetyl product is contrary to the thermodynamic ratio and proves that an equilibrated 1,3-diradical is not formed in these oxa-di-π-methane rearrangements.

Ultraviolet spectra for the compounds discussed in the last two sections are given in Table XVIII.

I. 3-Cyclopentenones

These species are unique in that both ends of the double bond are β to the carbonyl group. As mentioned earlier (section II.F.1), "normal" reactions of β,γ-unsaturated ketones are not observed, but instead decarbonylations generally occur.

Photolysis of 3-cyclopentenone in the gas phase (354 mm) at 313 nm gives butadiene and carbon monoxide with quantum yields of 0.83–0.94 at temperatures between 60 and 195°C.[116] Either an α-cleavage mechanism or a concerted cheletropic mechanism was considered possible. Although the efficiency of formation of α-cleavage products from 3-cyclopentenone is somewhat higher than that from cyclopentanone in the gas phase ($\Phi = 0.70$), the latter gives not only decarbonylation, but aldehyde formation as well.

The parent 7-norbornenone (**178a**) also undergoes decarbonylation to give 1,3-cyclohexadiene and 1,3,5-hexatriene, the latter from secondary photoreactions of 1,3-cyclohexadiene.[117] This reaction was not sensitized by benzophenone.
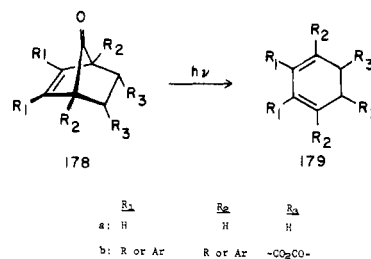
A variety of substituted 7-norbornenones are available from Diels–Alder reactions of cyclopentadienones, and these compounds undergo decarbonylation readily, apparently on either direct or acetone-sensitized photolysis.[118] The resulting cyclohexadienes often undergo a variety of secondary photoreactions. For example, the maleic anhydride adducts **178b** readily photodecarbonylate, and the resulting β,γ-unsaturated anhydrides undergo photolytic aromatization to the benzene derivative, CO, and CO_2.[118] The quantum yield for decarbonylation of the cyclopentadienone–maleic anhydride adduct is 0.54 at 257 nm.[119]

The less strained 3-cyclopentenones analogous to **178** do not decarbonylate readily. Thus, **180** undergoes no decarbonylation, but cyclization of the cis-stilbene moiety and oxidation to the phenanthrene occur upon photolysis in the presence of iodine or oxygen.[120] The unsaturated analog **181** undergoes a 1,5-shift to form **182** upon irradiation in acetone.[120]

TABLE XIX. Ultraviolet Spectra of 3-Cyclopentenones

Compound	λ_{max}, nm (ϵ)	Solvent	Ref
3-Cyclopentenone	258(8), 268(9), 278(11), 294(9), 300(11), 316(3), 325(3)	C_6H_{12}	116
178a	274(31)	C_8H_{18}	115
1,5,5-Trimethyl-2-bornen-7-one	270(58)	EtOH	a
1,2-(Tetramethylene)-2-norbornen-7-one	270(21)	EtOH	b

[a] J. J. Hurst and G. H. Whitham, *Proc. Chem. Soc.*, 116 (1961). [b] R. L. Cargill, B. M. Gimarc, D. M. Pond, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Am. Chem. Soc.*, 92, 3809 (1970).

180   181   182
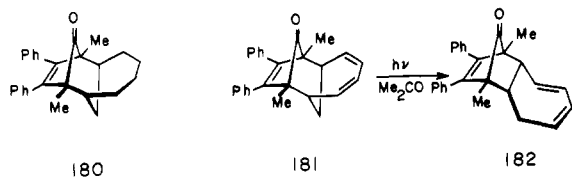
The simpler 3-cyclopentenones, **183**, have been studied in more detail. Starr and Eastman, in a study of substituent effects on ketone decarbonylations in solution, found that **183a** undergoes efficient decarbonylation to form the dienes shown,[121] while **183b** gives decarbonylation with a quantum yield of 0.02 upon irradiation in benzene.[122] This decarbonylation could be partially quenched by *cis*-piperylene, which was isomerized, indicating the reaction involves, at least in part, a triplet state of **183b**. In CH_2Cl_2, saturated hydrocarbons, or alcohol solvents, the epimeric photoreduction products **184** were formed in low yields, probably via triplet states, since piperylene and oxygen quenched their formation.

183   184

a: Me
b: H
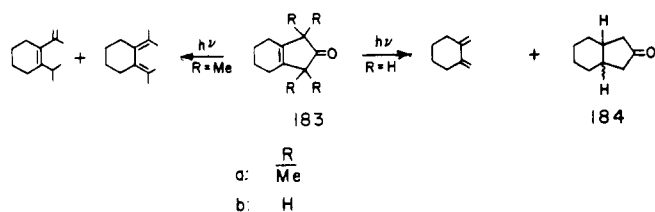
Turro and coworkers recently reported the stereochemistry of decarbonylation of **185** and **186**.[123] Both of these compounds decarbonylate via triplet excited states, as indicated by piperylene quenching of decarbonylation without an appreciable change of fluorescence intensity. In order to account for the relative quantum yields for product formation (shown below the figures), Turro and coworkers proposed competition between concerted linear and nonlinear cheletropic decarbonylation mechanisms, involving direct formation of the diene and CO ground states.[123] The relationship of this mechanism to the triplet reactions of other β,γ-unsaturated ketones is discussed in section IV of this review.

	R_1	R_2	c,c -187	c,t-187	t,t-187
185:	Me	H	Φ(313nm) 0.18	0.22	0.60
186:	H	Me	< 0.04	0.48	0.52
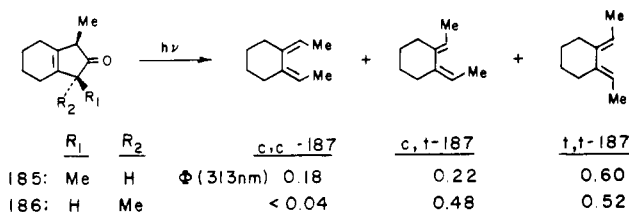
Table XIX gives the ultraviolet spectra of several 3-cyclopentenones. There is no enhancement of the $n\pi^*$ absorption in these molecules, regardless of whether the molecule is planar, as is 3-cyclopentenone,[124] or is highly puckered, as are the 7-norbornenones.

J. $\alpha,\beta,\beta',\gamma'$-Unsaturated and γ'-Keto-β,γ-Unsaturated Ketones

The compounds discussed in this section have both the

β,γ-unsaturated ketone moiety and an α,β-unsaturated ketone moiety present in the same molecule. Such systems might be expected to differ from those discussed earlier in that intersystem crossing is accelerated in α,β-unsaturated ketones.

1. $\alpha,\beta,\beta'\gamma'$-Unsaturated Ketones

a. Acyclic and Semicyclic

Tenny et al. reported the first example of a 1,2-shift in the acyclic acetophenone derivative **188a**.[125] Direct irradiation in benzene gave **189a**, along with numerous products formed by α-cleavage and recombination. The rearrangements of the variously labeled derivatives **188b–d** established the skeletal changes which occurred.

188   189   + a-cleavage products

	Ar	R	*
a:	Ph	H	^{12}C
b:	Ph	D	^{12}C
c:	Ph-^{14}C	H	^{12}C
d:	Ph	H	^{14}C
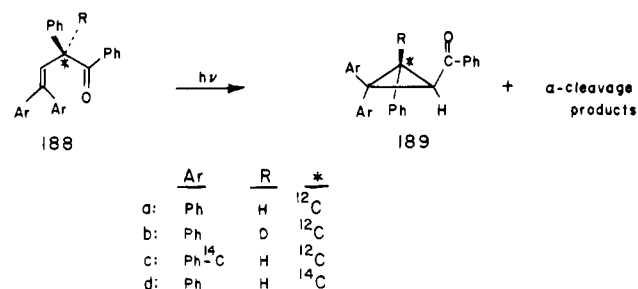
The unsubstituted parent of this kind of compound, 1,5-hexadien-3-one (**190a**), undergoes a photochemical intramolecular cycloaddition to give **191a** (30%) and two unidentified cyclopentanones.[126] Gibson and Erman studied a variety of methylated derivatives **190b–i**, which give variable yields (0–60%) of the bicyclic products **191b–i** as shown below **191**.[127] The intramolecular photocycloaddition represented by the conversion **190** to **191** is the intramolecular analog of the intermolecular α,β-unsaturated ketone photoannelation reac-

190   191
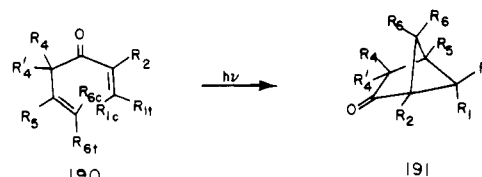
a: all R = H   (30-60%)
b: R_{1t}= Me, all other R's = H   (3%)
c: R_2 = Me,   "   (57%)
d: R_4 = Me,   "   (41%)
e: R_4 = R_4 = Me "   (0%)
f: R_{1t}= R_{1c}= Me "   (0%)
g: R_6 = Me,   "   (0%)
h: R_{6t}= Me, "   (56%)
i: R_{6t}= R_{6c}=Me "   (0%)
j: R_{1t}-R_2 = -(CH_2)_3-, R_6 = Me

192   193   194   195
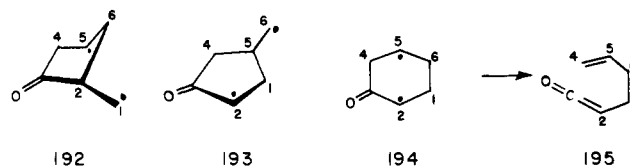
tion. The latter has been studied in some detail and appears to generally involve attack of the enone triplet ($E_T \sim 70$ kcal/mol) on the ground state of the alkene, followed by closure of the biradical to product.[128] The formation of **191** can be rationalized by initial formation of either of the "rule-of-five"[129] biradicals **192** or **193** followed by collapse to products. Similar results have been observed with 6-vinyl-2-cyclohexenone (see following section). In several cases, biradicals **194** are most likely formed, since photolysis of **190g** and **190l** in methanol gives esters, the result of trapping of ketenes **195**.[127] Since Gibson and Erman made no attempt to analyze low or high molecular weight products, competing type I, or II, or intermolecular reactions would not have been detected.[127]

Agosta and Smith found that the related compound **190j** gives exclusively the substituted ketene product **195**, resulting from initial six-membered biradical (**194**) formation.[130] These authors also found that irradiation of **190g** in methanol gave both **191g** in good yield (43%) and the ester formed by trapping of the ketene (27%) when a uranium glass filter was used to prevent product destruction.[130]

Erman and Gibson's study of optically active isopiperitenone (**196a**) and racemic 4-acetoxyisopiperitenone (**196b**) gave more details about the photochemistry of these systems.[131] Thus, irradiation of **196a** in cyclohexane gave optically active **197a** and recovered **196a** with no loss of optical activity. Irradiation in methanol gave both (+)-**197a** (25%)
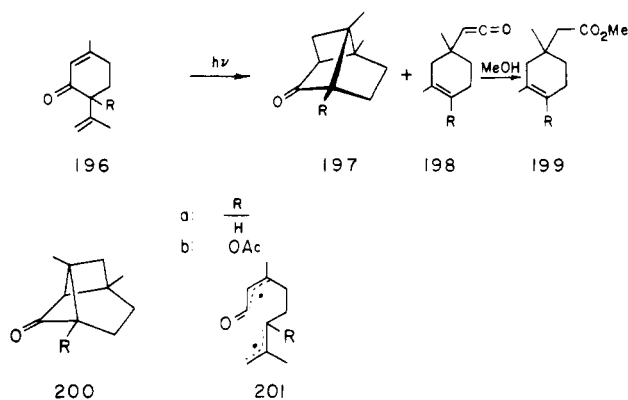
and racemic **199a** (49%). Similarly **196b** gave **197b** (42%) in cyclohexane and **197b** (15%) and ester **199b** (65%) in methanol. The ketene precursors **198** of **199a,b** could be detected by ir during irradiation in cyclohexane. The formation of **197** is rationalized on the basis of preferential formation of the five-membered ring biradical. Although the alternative intramolecular cycloaddition product **200** could fragment to the ketene **198**, this process would give optically active **199a**, whereas the **199a** formed is racemic. Therefore, an alternative process was suggested where **196** undergoes an α-cleavage process to give the achiral biradical **201**, which closes only to ketene **198** and does not revert to **196**, since no racemization of the latter is detected.[131] Similarly, biradicals such as **194** proposed by others as intermediates in similar transformations cannot be the sole intermediates, since they are chiral.

The related β,γ-unsaturated α-diketone **202** gives a single oxetane product **203**, upon direct irradiation.[132] Bishop and

Hamer suggested that the efficiency of this reaction ($\Phi \sim 0.6$) and the absence of hydrogen abstraction products may be a result of excited-state interaction between the diketone and alkene functions.[132]
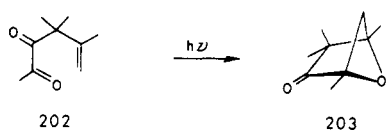
Schaffner and coworkers have investigated the 3-benzoyl-cyclopentenes **204**, analogous to the acetyl compounds **174** discussed earlier (section II.H.3).[133] Irradiation of optically active (R)-**204a** or **b** gave racemic **204** along with the α-cleavage, recombination products **205**, **206**, and benzaldehyde or anisaldehyde, respectively.[133] Photolysis of a mixture of **204b**

a: X = H
b: X = OMe
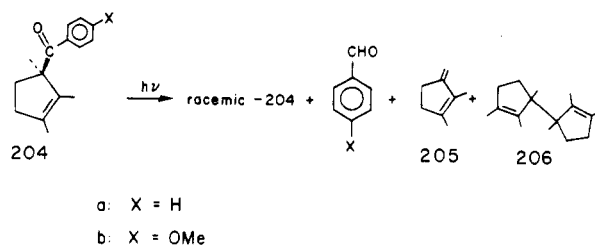
and deuterated **204a** gave crossed products, indicating that the formal 1,3-shift, which leads to racemization, is in large part the result of dissociation and radical recombination. Quantitative studies of rates of racemization, trapping of radical intermediates by CCl_4, and CIDNP revealed that the dissociation of **204a** or **b** occurred predominantly through triplet excited states, and that most of the "1,3-shift" arose from radical pair and noncage radical combinations.[133] Phosphorescence data for **204a** ($E_T = 74$ kcal/mol; $\tau = 5.5$ msec) and **204b** ($E_T = 70$ kcal/mol; $\tau = 105$ msec) indicate a lowest $n\pi^*$ triplet state for **204a**, and a $\pi\pi^*$ for **204b**.[114] However, the excitation in both of these states is doubtless localized more or less in the benzoyl moiety.

Singh and Ullman have investigated the chromophorically more complex $\alpha,\beta,\beta',\gamma'$-unsaturated ketones **207**.[134] These compounds are formed upon irradiation of the isoxazoles **208**. The reversible interconversion of **207** and **208** can be sensitized by acetone ($E_T \approx 80$ kcal/mol) or Michlers' ketone ($E_T = 62$ kcal/mol), but not by biacetyl ($E_T = 51$ kcal/mol). A very short-lived triplet is implicated, since piperylene does not quench the reaction. The conversion of **207** to **209** cannot be sensitized and occurs only upon high-energy ($\lambda \leq 313$ nm) irradiation. The latter transformation, involving initial CC cleavage to give a nitrile ylide, is characteristic of azirine excited states,[135] while the conversion of **207** to **208** requires a CN cleavage of the triplet excited state of the β,γ-unsaturated benzoyl moiety.

a: Ph
b: p-MeOPh
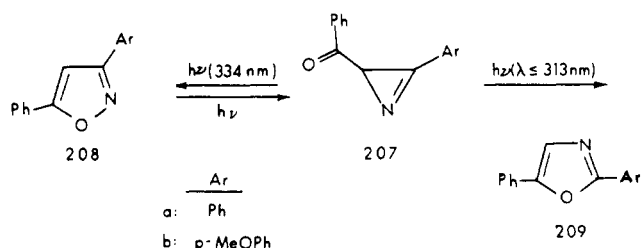
b. Cyclic

The photochemistry of 2,6-cyclooctadienone (**210**) has been studied independently by two groups.[136,137] Cantrell and Solomon[136] found that irradiation of **210** in aprotic solvents gave the tricyclic isomer **212**, presumably formed from the 1,3-shift product **211**, which was later isolated by Noyori et al.[137] This reaction was neither sensitized[136] nor quenched, implicating a singlet excited state precursor. Noyori et al. found that **211** was not formed upon direct irradiation with light of $\lambda > 350$ nm, suggesting that **211** is formed in an efficient α-cleavage reaction from an upper excited singlet of **210**. Noyori also detected **213** and **214** upon irradiation of **210** with unfiltered light in methanol. These esters can arise from the corresponding ketenes, which, like **211**, can be formed from collapse of an α-cleaved diradical.
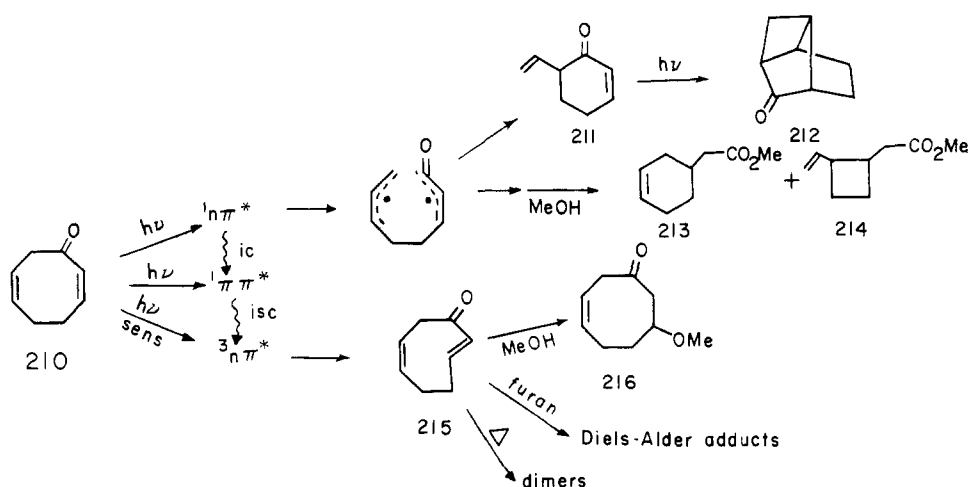
Figure 4. Products and postulated mechanism of 2,6-cyclooctadienone photochemistry.

The major product of irradiation of **210** is the trans isomer **215**, which can be detected by ir at low temperature,[136] and which dimerizes on heating or can be efficiently trapped with methanol (**216**) or with furan to give Diels–Alder adducts. Cantrell and Solomon propose that a triplet excited state leads to **215**, since **216** is the only product of irradiation of **210** in the presence of xanthone (E_T = 74 kcal/mol) as a triplet sensitizer.[136] Noyori et al. suggested that the $\pi\pi^*$ (or $n\pi^*$) singlets gave **212–214**, and the $\pi\pi^*$ triplet gave **215**.[137] The mechanism proposed in Figure 4 is a hybrid of those proposed by the two groups, and assumes that the $^1n\pi^*$ state is reactive, but slightly higher in energy than the $^1\pi\pi^*$ state (see section III.B.2) in methanol. In nonpolar solvents, the $n\pi^*$ state may be the lowest singlet, so that wavelength dependence would not be observed, except for a possible effect on rates of intersystem crossing.

The cyclodecadienone derivative **217** gives the 1,3-shift and cis,trans isomerized product **218** upon direct photolysis along with an unidentified ketene, detected by ir in the crude photolysate.[138] Germacrone (**219**), containing exocyclic α,β-unsaturation, undergoes cis,trans isomerization at both endocyclic β,γ and γ,δ double bonds upon acetophenone-sensitized photolysis.[139]
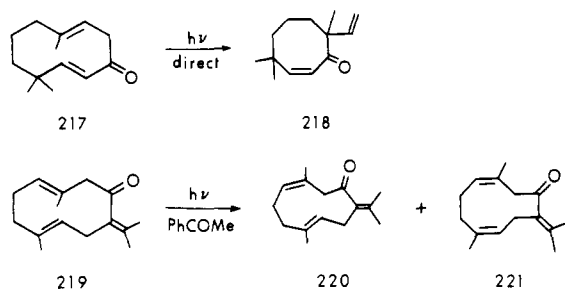
Finally, several Diels–Alder adducts of o-chloranil and alkenes undergo photochemical bis-decarbonylations to form 1,3-cyclohexadienes,[140] a reaction which most likely involves α-cleavage of the β,γ-unsaturated α-diketone system.

c. Bicyclic

i. Bicyclo[4.4.0] deca-4,10-dien-3-ones. Schaffner and co-workers investigated the steroidal dienones **222**.[141] Irradiation of the β-methyl dienone gave two cis-fused di-π-methane products **223**. One of these had the β-methyl-a cis to C-b, while the other had an α-methyl-a trans to C-b. The α-methyl isomer of **222** gave two di-π-methane products, one with a β-methyl trans to C-b and the other with an α-methyl cis to C-b. Both epimers of **222** also gave the 1,3-alkyl shift prod-

ucts **224**.[141] Both of these reactions are unusual for these systems, since reactions characteristic of the 1,4-diene system, rather than of the β,γ-unsaturated ketone system, are observed.
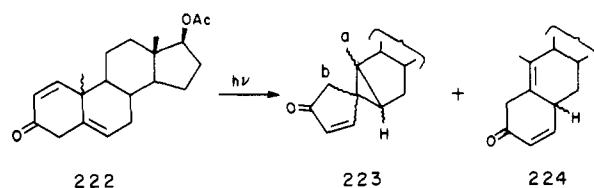
ii. Bicyclo[4.2.0] octa-3,7-diene-2,5-diones. A number of p-benzoquinone photoadducts with acetylenes have been investigated. Anet and Mullis reported the photochemically irreversible 1,3-shift of **225a** to give **226a** (55%), and oxetane formation to give **227** (20%).[142] The deuterated analog **225b** rearranged to **226b**, revealing the 1,3-shift nature of the skeletal rearrangement.

	R	R_1	R_2	R_3	R_4
a:	H	MeO	Ph	H	H
b:	H	MeO	Ph	D	H
c:	benzo	Ph	Ph	H	H
d:	benzo	Me	Me	H	H
e:	benzo	Me	H	H	H
f:	benzo	Me	Me	H	Me
g:	benzo	Me	H	H	Me
h:	benzo	Me	Ph	H	Me
i:	benzo	Me	Me	Ph	H

Similar results in the naphthoquinone series have been reported.[143] The compounds **225c–h** undergo irreversible 1,3-shifts to give **226c–h**.[143] In the case of **225i** and **226i**, a photostationary state of 1:5.3 was formed. In spite of the fact that the extinction coefficients for **225c–h** are similar (ϵ_{366} 1300–1500) at the wavelength utilized in the photolysis, photostationary states were not formed in these cases. This phenomenon was attributed to a mechanism involving α-cleavage, recombination, the former occurring readily only when an α-methyl or α-phenyl group was present to stabilize the intermediate.[143]

iii. Bicyclo[3.2.0] hepta-3,6-dien-2-ones. Although the photochemical conversion of bicyclo[3.2.0]heptadienones **228** to isomers with the same carbon skeleton (**229**) is similar to the Büchi–Burgess 1,3-shift of the corresponding 3,4-dihydro

compounds, the mechanisms of these apparently identical reactions are quite different. The ring system 228 is obtained upon irradiation of corresponding tropolone derivative. Upon further irradiation, 228a–d give 229a–d.[144] These enol ethers are readily hydrolyzed with ring opening to oxocyclopentylacetic esters. Similarly, 228e and f (likely intermediates in photolyses of the corresponding chlorotropolones) form 229e and f on photolysis.[145] However, the isomeric 228g gives only dimers upon irradiation. The corresponding products of acylaminotropone photocyclizations (228h,i) also undergo the rearrangement,[146] as does the probable intermediate in the photolysis of O-methylpurpurogallin.[147]

230

229

231
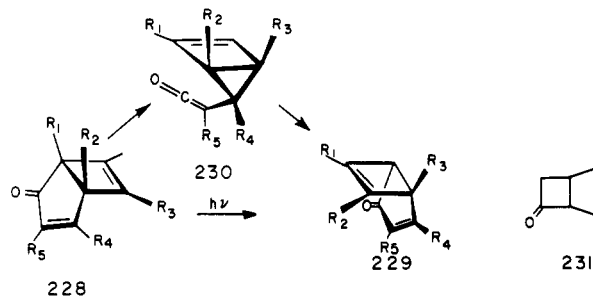
228

	R_1	R_2	R_3	R_4	R_5
a:	OMe	H	H	H	H
b:	OMe	Me	H	H	H
c:	OMe	H	H	Me	H
d:	OMe	^iPr	H	H	H
e:	OMe	Cl	H	H	H
f:	OH	Cl	H	H	H
g:	H	H	Cl	H	OH
h:	NHCOMe	H	H	H	H
i:	NHCOPh	H	H	H	H
j:	OMe	H	H	(OMe,OMe,OMe)	H
k:	H	H	H	(OMe,OMe,OMe)	H
l:	OH	H	H	H	H

The mechanisms of these rearrangements were elegantly elucidated by Chapman and coworkers by low-temperature photolysis. Irradiation of 228a at 77°K led to a ketene, detected by ir, formulated as 230a.[148] This ketene is stable below −180°C, but reverts to 228a and 229a upon heating to −70°C. The ketene intermediate can also be photochemically converted to products. Thus, the photoreactions of 228 and 229 are [3,3] sigmatropic shifts[149] and proceed through singlet states, since sensitized photolysis of 228a gives a different product, 229k.[150]

Further evidence for the intervention of ketene intermediates comes from photolysis of the tropolone photoproduct 228l. Direct photolysis in hexane gives the diketone corresponding to 229l, as well as the diketone 231.[150] The latter could be formed from ketene 230l, which has been detected spectroscopically.[151]

The reactions of these systems appear to involve either initial α-cleavage, followed by collapse to 230, or initial di-π-methane type bridging, or a concerted reaction which is equivalent to the simultaneous operation of both these bonding changes. Although these bicyclic systems are particularly prone to undergo this formal [3,3] sigmatropic shift, the reaction is also observed with a number of acyclic $\alpha,\beta,\beta',\gamma'$-unsaturated ketones, as noted earlier.

iv. Bicyclo[3.2.1]octa-3,6-dien-2-ones. The behavior of these systems is similar, in part, to that of the compounds discussed in the preceding section. Thus, the parent 232a undergoes the photochemical [3,3] shift to form the ketene 233a, at −196°.[152] The ketene can be trapped with methanol (234a) or reverts to 232a upon warming. The fully substituted derivatives 232b and c give cyclobutanones 235b and c upon direct photolysis, even in the presence of nucleophiles.[153] The failure of nucleophiles to intercept 233b and c

234

232 233 235

236
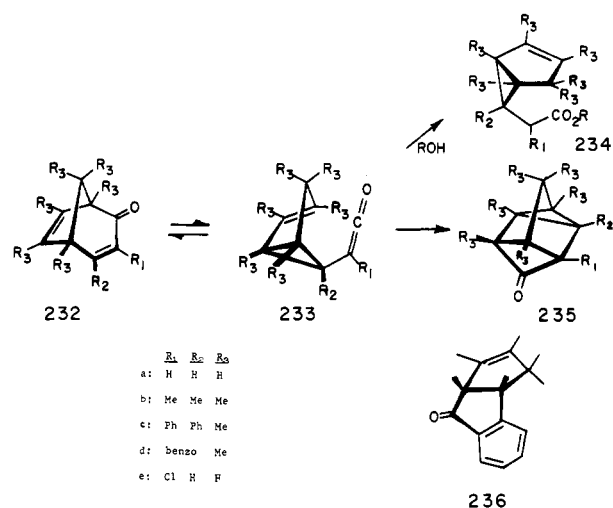
	R_1	R_2	R_3
a:	H	H	H
b:	Me	Me	Me
c:	Ph	Ph	Me
d:	benzo		Me
e:	Cl	H	F

presumably arises from steric hindrance and decreased electrophilic reactivity of the ketene caused by alkyl or aryl substituents. The chloro derivative 232e reacts analogously to give the cyclobutanone 235e.[154] However, the intermediate ketene 233e can, in this case, be trapped by water or methanol to give the acid derivatives 234e. The formation of the cyclobutanone in this case is attributed to the greater cycloaddition reactivity of the haloketene over the aldoketene 233a.[154] The benzo derivative 232d gives a 1,3-shift and formation of photostationary state with 236.[155]

v. Bicyclo[3.2.2]octa-3,6-dien-2-ones. The first rearrangement of a system of this type was discovered by Kende and coworkers.[156] Photolysis of the tropone–benzyne adduct 237a in water gave the acid 242a, while photolysis in acetonitrile gave 241a, which must arise from the 1,3-shift product 240b.[156] The different behavior in the last two solvents was rationalized in the following way: the efficient [3,3]-shift of 237a to 238a is thermally reversible, so that in the absence of a nucleophile, 242a is not observed. In that case, the less efficient 1,3-shift to form 240a is the only detectable reaction.[156] Chapman and coworkers were able to detect the ketene 238a as the major product of photolysis of 237a at low temperature.[152] Methanolysis of 238a at −80° gave only the endo ester of 242.[152]

Kende and Goldschmidt found that the benzophenone-sensitized photolysis of 237a gave the di-π-methane rearrangement product 239, rather than an oxa-di-π-methane product which would have the reversed connectivity of the α,β-unsaturated ketone moiety.[157]

Chapman reported the facile [3,3]-shifts of several other ketones of this type. Thus, 237b and 237c are rapidly converted into the ketenes 236b and c, and 238b readily undergoes electrocyclization at −80° to form 7-cycloheptatrienyl-ketene.[152] The tropone–azo diester adducts 237d–f give esters 242d–f arising from the [3,3]-shift products, 238.[158] In the case of 237d an additional product, 243, was formed, said to arise from a [3,3]-shift involving the N–N bond.[158] Adducts 237g, h, and i[159] also give esters arising from [3,3]-shift products, 238. However, the tropolone adducts 237j and 237k and the dibenzo compound 237l give the 1,3-shift products arising from 240.[160] The latter are believed to arise from excited triplets, since the reaction occurred even in very dilute solution in acetone. The reaction also occurred in THF with or without added piperylene.[160] A number of other adducts similar to 237h have recently been shown to undergo [1,3] and [3,3]-shifts.[161] Finally, the singlet oxygen adducts 237m of a number of tropones have been photolyzed. The suggested mechanisms involved an initial [3,3]-shift followed
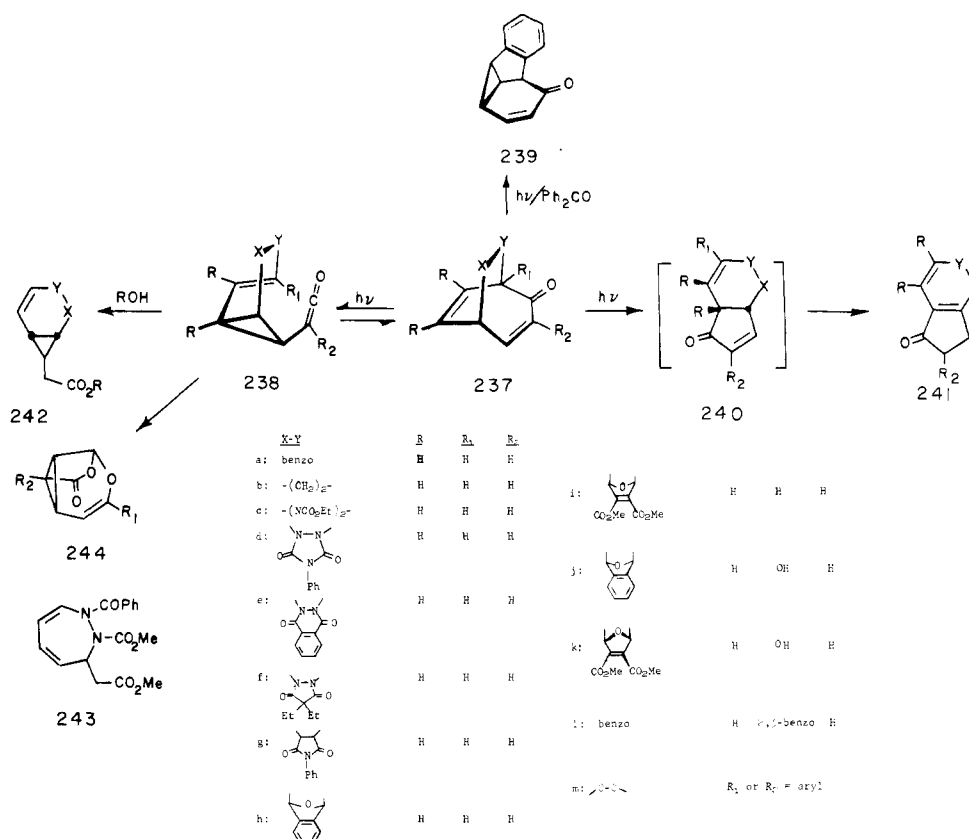
by subsequent thermal reactions to give **244m** in very low yields.[162]

A rearrangement of a monocyclic analog of those noted above was reported recently. Thus the azepinone shown in the drawing undergoes a photochemical [3,3] sigmatropic shift to form an isocyanate upon direct irradiation.[163]
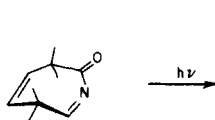
d. Conjugated Cyclopolyenones

i. Cyclobutenones. The cyclobutenones are unique systems in which one end of the double bond is β to the carbonyl, and the other is α. The photochemistry of these species once again involves α-cleavage. For example, Chapman and Lassila observed the formation of the vinyl ketene **246a** upon irradiation of **245a** at low temperatures.[148] Baldwin and McDaniel studied the stereochemistry of the photochemical and thermal ring openings of the cyclobutenones **245b–d**.[164] A remarkable result was obtained. In the photochemical reaction, the isomers **246b–d** were obtained, while the opposite stereochemistry was found in the thermal reaction. The results indicate α-cleavage with some excited state preference for one mode of rotation.[164] A similar ring opening is also ob-

served with benzocyclobutenone **245e**.[165] Trindle suggested that a group with p orbitals at C-4 was required for allowed opening of the cyclobutenone.[166]

ii. 2,4-Cyclohexadienones. The photochemistry and spectroscopy of these compounds have been reviewed recently[167] and will be discussed here only when the results are relevant to interpretations of the photochemistry of simpler β,γ-unsaturated ketones. Figure 5 summarizes the various general reactions which are known for these species. Irradiation of simple 2,4-cyclohexadienones **247**, in the presence of nucleophiles gives the dienyl acid derivatives **250**. The dienyl-ketenes **249**, which were proposed as intermediates in the first reported examples of this reaction,[168] have been observed spectroscopically by low-temperature irradiation[148,167] and are found to revert thermally to the starting cyclohexadienones.

By carrying out the reaction in a highly polar solvent, or upon ring methylation of the cyclohexadienone, the reaction takes a different course, giving **248**,[167,169] an oxa-di-π-methane product. Since these ring substitution and solvent polarity

Figure 5. Summary of 2,4-cyclohexadienone photochemistry.
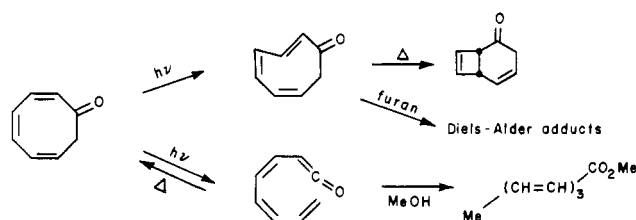
Figure 6. Photochemistry of 2,4,6-cyclooctatrienone and 2,3-homo-tropone.

changes are expected to lower the energy of the $\pi\pi^*$ excited state compared to that of the $n\pi^*$ excited state, Hart suggested the difference in reactivity is explained by invoking an $n\pi^*$ singlet for the ring-opening formation of **249** and a $\pi\pi^*$ singlet for the oxa-di-π-methane rearrangement. This explanation is supported by marked changes in absorption spectra as solvent polarity is changed. Thus, hexamethyl-2,4-cyclohexadienone has $\pi\pi^*$ and $n\pi^*$ bands at 302 nm (ϵ 4800) and 354 nm (ϵ 120), respectively, in hexane, but in trifluorethanol, a broad $\pi\pi^*$ band at 318 nm obscures the $n\pi^*$ band.[169] The singlet nature of both of these rearrangements is suggested by the failure of attempted sensitization and quenching.

The similarity of these reactions to those of simpler β,γ-unsaturated ketones is striking, while the differences are revealing. Thus, the electrocyclic ring opening is an α-cleavage, reminiscent of the $^1n\pi^*$ reactions of β,γ-unsaturated ketones, while the oxa-di-π-methane rearrangement, the common β,γ-unsaturated ketone triplet reaction, is thought to involve the singlet π,π^* state in 2,4-cyclohexadienones. As will be discussed later, it is probable that oxa-di-π-methane reactions typically involve $\pi\pi^*$ excited states.

Finally, Hart and coworkers have found that the formal oxa-di-π-methane product **248** can be formed by thermal cyclization of the dienylketene **249** in the cases of sterically encumbered compounds such as hexamethyl-2,4-cyclohexadienone.[170]

iii. Bicyclo[4.1.0]hept-4-en-2-ones. Although this class of compounds differs from those discussed in this section, their similarity to those discussed in the previous section and major differences from the formally similar 3-cyclohexenones warrant their inclusion here.

Bellamy and Whitham found that irradiation of **251a** in the presence of cyclohexylamine gave **253a** ($X = NHC_6H_{11}$).[171] The ketene intermediate **252a** was proposed. Baldwin and Krueger investigated a labeled compound **251b** and found the reaction was highly stereoselective, with the endo methyl ending up cis (**253b**), which implied that the ring opening of **251b** to **252** was stereospecific.[172] The stereospecificity was confirmed by Bellamy and Crilly;[173] however, these authors suggested that the assignments shown in drawings **251bc–253bc** were correct, and that Baldwin's initial assignments for all four compounds should be reversed.[173-174] Bellamy and Crilly also studied the benzyl compound **251d** and found a similar stereochemical course.[173] They suggested that α-cleavage was followed by rotations which minimized steric
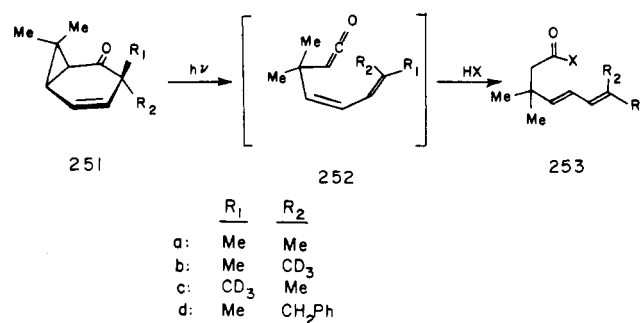
repulsions between R_1 or R_2 and the cyclopropyl methyls, and that the second step of the reaction involved cyclopropane ring cleavage.[174]

iv. 2,4,6-Cyclooctatrienones. These species incorporate a triene system which is conjugated with the carbonyl group on one end and β to the carbonyl group on the other end. Büchi and Burgess reported the photochemistry of 2,4,6-cyclooctatrienone in 1962.[175] Irradiation in methanol gave methyl octatrienoates, while irradiation in pentane gave bicyclo[4.2.0]octa-4,7-dien-2-one. Chapman and coworkers applied their low-temperature photochemical techniques to this reaction and discovered the course of events shown in Figure 6.[176] Irradiation gives both the α-cleavage (or electrocyclic reaction) product, hexatrienylketene, and the cis,trans isomerization product. The latter is thermally converted to the bicyclic ketone, or can be trapped by furan, while the ketene thermally reverts to cyclooctatrienone, or can be trapped by methanol. The result is significant in comparison to 2,4-cyclohexadienone photochemistry. In the latter, $n\pi^*$ states give ketene formation by α-cleavage, while $\pi\pi^*$ states give the oxa-di-π-methane rearrangement. In the eight-membered ring, the potential 1,2-shift product, 2,3-homotropone, is absent, but the trans trienone is formed. This cis,trans isomerization is, however, a reaction characteristic of $\pi\pi^*$ states, but would not be expected in a six-membered ring. Paquette and Cox have studied the photochemistry of 2,3-homotropone.[177] Although it does undergo photochemical conversion to 2,4,6-cyclooctatrienone, several additional products formed make it unlikely that 2,3-homotropone could have been overlooked in the studies of 2,4,6-cyclooctatrienone.

The available ultraviolet spectra of the $\alpha,\beta,\beta',\gamma'$-unsaturated ketones discussed here are given in Table XX. All show strong $\pi\pi^*$ absorptions and only slightly intensified $n\pi^*$ transitions.

2. δ-Keto-β,γ-unsaturated Ketones

a. Bicyclo[4.4.0]dec-1-ene-3,9-diones and Related Systems

An early example of a 1,2-shift upon irradiation in acetone is represented by the rearrangement of the steroidal system **254** to **255**.[178] The 1,2-shift of **256a** was found to proceed
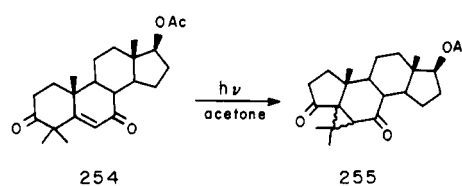
through a triplet state of the ketone, since naphthalene could completely quench the reaction.[178] Both epimers were produced from **256a**, and all four were produced from **256b**.[179] A stepwise mechanism involving intermediates **258** and **259**
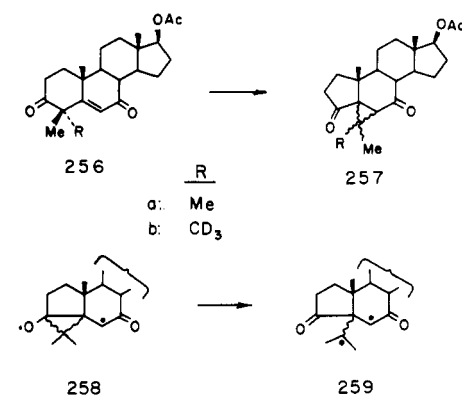
TABLE XX. Ultraviolet Spectra of α,β,β',γ'-Unsaturated Ketones

Compound	λ_{max}, nm (ϵ)		Solvent	Ref
	ππ* transition	nπ* transition		
202		431(39)	C_5H_{12}	132
204a	237(10000), 271(835)	329(120)	C_8H_{18}	133
	244(9700), 265(1500)	326(166)	EtOH	133
204b	265(16300)	329(141)	C_8H_{18}	133
	275(13000)	323(290)	EtOH	133
210	227(7200)	320(75)	MeOH	136
222 (α-CH₃)	230(10700)	337(82)		141
222 (β-CH₃)	227(11500)	329(128)		141
225a	382(1260)	450(2)	$CHCl_3$	142
226a	382(6310)	450(100), 500(4)	$CHCl_3$	142
228a	224(6600)		EtOH	144
228b	230(6310)		H_2O	144
229b	226(6420)		95% EtOH	144
229c	233(9730)		95% EtOH	144
2,4,6-Cyclo-octatrienone	210(2300)	288(110)	EtOH	175

was proposed to account for the stereochemical results. The intermediacy of 259 in this case is perhaps surprising, since the work of Givens and coworkers apparently ruled out this type of intermediate in the bicyclo[2.2.2]octenone 1,2-shift (section II.D). The work of Nakanishi described earlier suggested the same type of intermediate, however. The lowest triplet of 256a was found by emission spectroscopy to have an E_T of 72.4 kcal/mol and a lifetime of 32 msec,[178] indicating a ππ* triplet as the lowest triplet state. The phosphorescence quantum yield of 0.43 reflects the efficient intersystem crossing of 256.

A simpler system of this type, 260, undergoes both α-cleavage and intramolecular hydrogen abstraction to form 262 and a 1,3-shift leading ultimately to 261. Both of these reactions occur on direct irradiation.[180] The difference be-

260

261

262
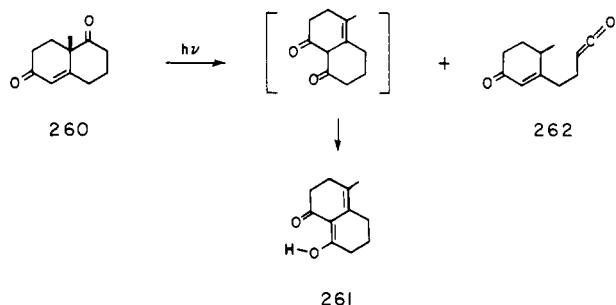
tween the photochemistry of 256 and 260 is somewhat perplexing, but in light of the quantum efficiency of the triplet reaction, the difference probably arises from enhanced propensity of 260 to undergo α-cleavage, presumably from an nπ* singlet before intersystem crossing.

The bis(α,β-unsaturated) ketone 263, which is simultaneously an α,β- and a β,γ-unsaturated ketone, undergoes a photochemical rearrangement to 264 upon direct irradiation, or upon sensitized irradiation using sensitizers of $E_T \geq 65.5$ kcal/mol.[181] Partial quenching by 1,3-cyclohexadiene was also observed. This reaction is a di-π-methane reaction, formally involving only the 1,4-diene unit.

263

264
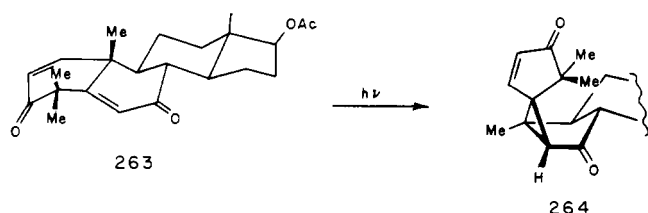
b. Semicyclic

Matsuura and Ogura reported that the acylcyclopentenone 265a undergoes a 1,2-shift to form the exo isomer of 266a upon direct irradiation.[182] However, Plank and Floyd found that the endo isomer shown, 266b, was formed upon irradiation of 265b, and these authors suggested the same stereochemistry for the photoproduct formed from 265a.[183]

265

266

	R
a:	ᵗBu
b:	Ph
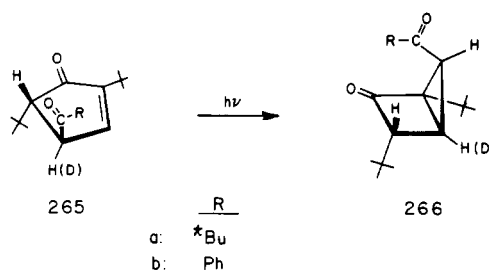
c. Bicyclo[3.3.1]nona-3,7-diene-2,6-diones

Mellor and coworkers have discovered both 1,2- and 1,3-shifts in these systems. The parent system, 267a, undergoes conversion to both the triasterane 268a and the dihydrocoumarin 270, which was isolated as coumarin.[184] The formation of 270 involves an unusual 1,5-acyl shift, while the formation of 268a could involve either two 1,2-acyl shifts, typical of β,γ-unsaturated ketone triplets, or two successive 1,2-alkyl shifts, characteristic of α,β-unsaturated ketones.[185] The photolysis of the substituted analog 267b gave the triasteranedione 268b, which must arise from two successive 1,2-acyl shifts. The 1,3-shift product 269b (two epimers) was also formed from 267b.[184] The sulfur analog of these compounds 267c undergoes only a 1,3-shift, and "preliminary studies do

267

268

269

	R	X
a:	H	CH₂
b:	Me	CHPh
c:	H	S

270
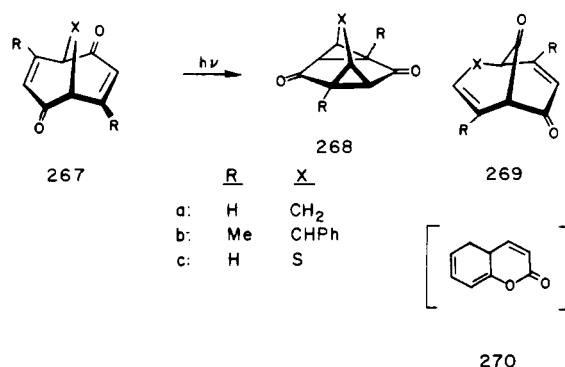
TABLE XXI. Ultraviolet Spectra of γ-Keto-β,γ-unsaturated Ketones

Compound	λ_{max}, nm (ϵ)		Solvent	Ref
	$\pi\pi^*$ absorption	$n\pi^*$ absorptions		
256a		sh296(33)	C_6H_{12}	178
		293(44)	EtOH	
260a	229(80000)	349(560)	EtOH	184
267b	237(15700)	348(758)	EtOH	185
267c	239(6910), 267(2775)	311(164), 340(166), 359(337), 378(470), 414(244)	C_6H_{12}	185
	240(6820), 262(3380)	310(273), 336(240), 350(371), 368(458), 413(344)	EtOH	185

not conflict with the view that the photoreaction proceeds via the singlet state".[185]

More recent studies of **267b** and analogs with substituents on the phenyl group have been reported.[186] The formation of **268b, 269b** (two epimers), and a product resulting from a single oxa-di-π-methane rearrangement of **267b** involved triplet states in every case, since formation of all products could be quenched by piperylene and sensitized by acetone. Thus, both the 1,3-acyl shift to give **269**, and the 1,2-shifts involve triplets; phosphorescence measurements (λ_{max} 485 nm, τ ~3.4 msec) on **267b** suggested that $n\pi^*$ triplets were involved.

Spectroscopic data for this series of compounds is given in Table XXI. Strong $\pi\pi^*$ absorptions and moderately enhanced $n\pi^*$ transitions are observed.

3. Bichromophoric Molecules Containing Both β,γ- and α,β-Unsaturated Ketones

a. Cyclopentadienone Dimers

Cyclopentadienone dimers are 7-norbornenones containing an appended α,β-unsaturated ketone moiety. While photochemical decarbonylation is the principal fate of simple 7-norbornenones (section II.I), a variety of different photochemical reactions have been observed with the cyclopentadienone dimers. The parent compound **271** undergoes conversion to the [2 + 2] cage, **272**, and the 1,3-shift product **273**, in a ratio of 96:4 upon either direct or sensitized irradiation.[187,188] Naphthalene quenched the formation of both products with the same efficiency, indicating that a common triplet state leads to both **272** and **273**.[188] These reactions are photochemically reversible; independent photolysis of **274** gave

Fuchs reported that the diphenylcyclopentadienone dimer **275a** undergoes a photochemically reversible 1,3-shift to **276**.[189] Sensitization and quenching experiments were equivocal about the excited state involved. Warrener and coworkers reported without details, that the dimethyldiphenylcyclopentadienone dimer **275b** underwent photolysis in acetone to form **277b**.[191] However, Fuchs found that irradiation of **275b** in dioxane at λ >300 nm gave a different cage compound, tentatively identified as **278**, and on this basis Fuchs concluded that **275b** was actually the exo-cyclopentadienone dimer.[189] Recently, Fuchs and Pasternak have proven that **278** is the correct structure of the long wavelength cage compound.[190] In our laboratories, further complexities were revealed.[192] The compound **278** was isolated upon photolysis at 350 nm in several solvents, but photolysis at 254 nm in acetone gave the Warrener cage **277b**.[192] We concluded that the latter compound was formed from a triplet state of **275b**. However, in a caustic attack on our work and a correction of his earlier work, Fuchs disputed our claim of sensitization and reported that an acetone filter was sufficient to produce conversion of **275b** to **277b**.[193,194] We found that irradiation of **275b** in acetonitrile at 254 nm did not give **277b**, but resulted in decarbonylation to form **280b**.[192] Furthermore, direct irradiation of **275a** at 254 nm in acetonitrile or acetone gave **280a**, while at 350 nm, Fuchs' 1,3-shift results were duplicated. The endo structure of **275b** was also proved in our laboratories,[192] and later in Fuchs',[193] by formation of an alcohol corresponding to **277b** by photolysis of the alcohol formed by reduction of the bridged carbonyl in **275b**. We also found that irradiation at 350 nm of **275b** in the crystalline state gave 43% of **277b** and 15% of **278b**.[192] Fuchs extended these observations to several other dissociating cyclopentadienone

273   271   272

274

271, 272, and 273, and the formation of 274 from 271 in low efficiency was shown indirectly.[188] The interconversions of 271, 273, and 274 are all intramolecular 1,3-shifts which could involve a common biradical intermediate. Attempted trapping of such an intermediate by a nitroxide was unsuccessful.[188]

280   276   275   277   278   279

a: H
b: Me
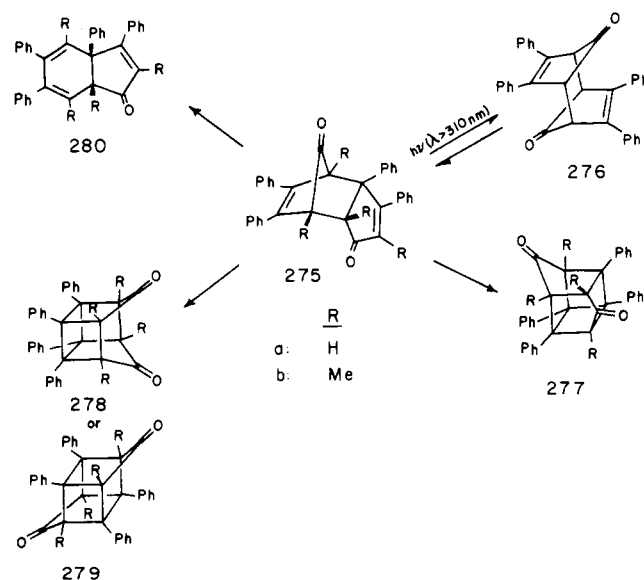
TABLE XXII. Ultraviolet Spectra of
$\beta,\gamma,\delta,\epsilon$-Unsaturated Ketones

Compound	λ_{max}, nm (ϵ)		Solvent	Ref
283	208(4000)	275(150)	EtOH	198
285	210(~6000)	~285(~150)	EtOH	198
(E)-287a	235(18450)	277(1010)	EtOH	198
(E)-287b	238(19700)	285(1180)	EtOH	198
(E)-287c	235(25200)	274(2500)	EtOH	198
(E)-287d	239(15000)	280(2000)	EtOH	198
(E)-287e	240(19600)	285(340)	EtOH	198
(E)-287f	237(17200)	280(1330)	EtOH	198
(E)-287g	239(9200)	280(1540)	EtOH	198
(Z)-287f	238(10260)	280(1300)	EtOH	198
(Z)-287g	236(11200)	280(720)	EtOH	198

dimers.[9][14] The origin of **278** remains an intriguing problem which has not yet yielded to mechanistic studies.

In the context of β,γ-unsaturated ketone photochemistry, the cyclopentadienone dimer results are of interest for the following reasons: the parent compound **271** appears to give mainly intersystem crossing to form a triplet state which either undergoes intramolecular [2 + 2] photocycloaddition, or cleavage of the σ-bond β to both the bridging carbonyl and to the α,β-unsaturated ketone double bond. These reactions are analogous to other α,β-unsaturated ketone triplet reactions.

The substituted compounds appear to undergo the intramolecular [2 + 2] cycloaddition from an α,β-unsaturated ketone triplet, but the β-cleavage may occur from either a singlet or triplet state. The decarbonylation reaction, which is analogous to known 7-norbornenone reactions (section II.I) probably occurs from the 7-norbornenone nπ^* singlet state. This may be the second excited singlet state of this molecule, although the evidence is not yet conclusive.

b. 2,4-Cyclohexadienone Dimers

Becker and Konar reported that irradiation of the cyclohexadienone dimers **281a–f** with light of λ >310 nm gave the [2 + 2] caged adducts **282**,[195] which are normal α,β-unsaturated ketone triplet reaction products.

	R_	R_	R_	
a:	OH	Me	H	
b:	OH	Me	Me	
c:	OH	H	Me	
d:	OAC	Me	Me	
e:	OAC	Me	h	
f:	PhCH_	Me	H	
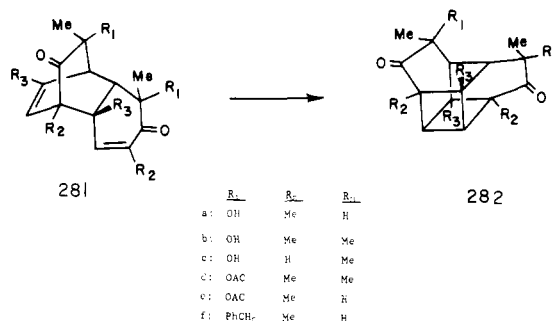
K. $\beta,\gamma,\delta,\epsilon$-Unsaturated Ketones

1. Semicyclic Dienones

The direct irradiations of a number of linear 3,5-heptadienones in which part of the chromophore is incorporated in a ring have been studied by van Wageningen and Cerfon-
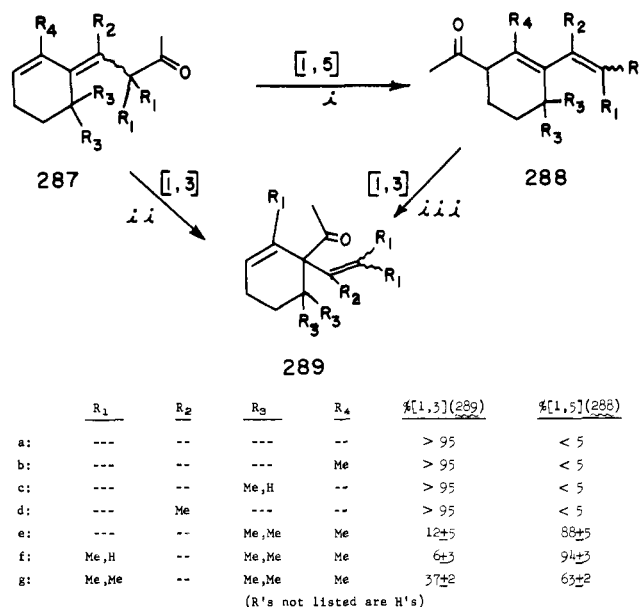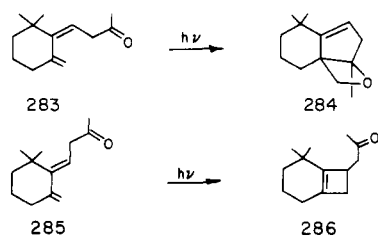
Figure 7. Photochemical reactions of $\beta,\gamma,\delta,\epsilon$-unsaturated ketones.

tain.[196-198] The compounds containing the s-cis diene moiety undergo oxetane formation (**284**) or electrocyclization to the cyclobutene (**286**) depending on the initial β,γ-double bond geometry. As shown in Table XXII, these compounds must have twisted diene units and little interaction between carbonyl and diene functions. The photochemical behavior of these compounds resembles that of isolated ketone and diene moieties.

When the diene moiety is constrained to an s-trans configuration, 1,3- or 1,5-shifts occur. Figure 7 summarizes the photochemistry of these species. Alongside the identification of the compounds **287–289** are listed the photochemical reactions which have been observed, extrapolated to zero conversion.[199] The yields given are for the E isomers, but the results starting with the Z isomers were essentially identical. Compounds **288e,f** give 1,3-shifts to form **289e,f** upon direct irradiation. The most notable feature of the tabulation of photochemical reactions given in the drawing is that the substituents R$_3$ have a major influence on the course of the reaction. The compounds with both R$_3$'s equal to methyl undergo the 1,5- and 1,3-shifts, while if one or both R$_3$ equal hydrogen, the 1,3-shift is the nearly exclusive reaction.[198,199] While quantum yields are really required to make deductions about the effect of the gem-dimethyl group, it is possible that compounds **287a–d** which are not sterically crowded can achieve a conformation for concerted 1,3-shift, while the remaining compounds react via α-cleavage–recombination or via a conformation in which acyl-C-5 bonding is possible. However, it appears unlikely that a concerted 1,5-acyl shift could occur across the rather large distance separating the ϵ and carbonyl carbons. Upon sensitized irradiation of these compounds, cis,trans isomerization occurs to the exclusion of other reactions. The dependence of the cis:trans photostationary state as a function of sensitizer E_T parallels the data obtained for piperylene, implying the involvement of a normal diene $\pi\pi^*$ triplet state.[199] A wavelength dependence was also observed upon direct irradiation; upon 300-nm irradiation, cis,trans isomerization occurs to a small extent, but at 254 nm, this reaction is nearly as efficient as the acyl shifts. The authors propose that intersystem crossing to the diene triplet state occurs from an upper singlet at 254 nm.[199] This conclusion apparently requires excitation of a diene singlet at 254 nm, which, however, is not expected to intersystem cross. We suggest the alternative in which a geometry unsuitable for α-
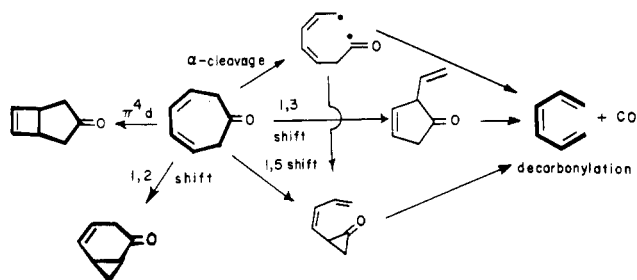
Figure 8. Observed (boldface) and hypothetical reactions of 3,5-cycloheptadienones.

cleavage is excited at 254 nm, and this (nπ*) singlet intersystem crosses and transfers triplet excitation to the noninteracting diene moiety.

In previous sections, a 4-phenyl-3-cyclohexenone, **80h**, was discussed. Compound **80h** is similar to **287** in that 1,3-shifts are observed upon direct irradiation of both, but the oxa-di-π-methane rearrangement occurs upon acetophenone sensitization of **280h**, and only cis,trans isomerizations occur with the flexible **287**.

The cyclic $\beta,\gamma,\delta,\epsilon$-unsaturated ketones **290a,b** are systems in which 1,5-shifts seem more likely. However, photolysis gives only the 1,3-shift products. Xanthone-sensitized irradiation of **290a** gives the 1,3-shift product also.[200]

290

	R
a:	Me
b:	Ph
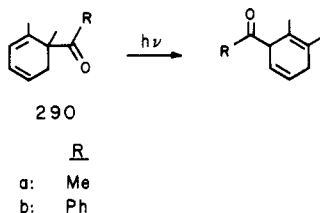
A more complex $\beta,\gamma,\delta,\epsilon$-unsaturated carbonyl was studied by Jones and Kneen.[201] They found that the β,γ-saturated dienyl imides **291** undergo electrocyclizations, 1,5-shifts (**292**), and 1,2-shifts (**293**).[201] Similar anhydrides cited earlier (section II.I) fragment to form the aromatic systems without rearrangement.

291

292

	R₁	R₂
a:	Ph	H
b:	Me	H
c:	H	H

293
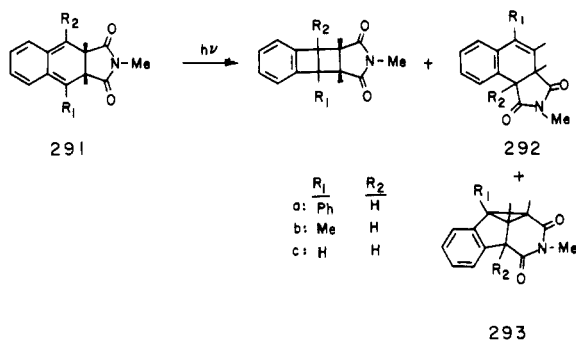
The $\alpha,\beta,\beta',\gamma',\delta',\epsilon'$-unsaturated ketone **294** undergoes a reaction reminiscent of the bicyclo[3.2.0]hepta-3,6-dien-2-ones, namely, formation of the cyclopropylketene **295**, which can be trapped with methanol.[188] This reaction, as well as those of the [3.2.0] systems, may be initiated either by an α-cleavage or by primary 4–6 bonding. Appreciable interaction of the two chromophores in **294** is indicated by its ultraviolet spectrum [λ_{max} nm(ϵ) 220(9800), 265(2400), 327(213) as compared with the models 1,3-cyclohexadiene [259(10,000)] and 2-cyclopentenone [218(7250), 305 (32)].[188]

294

295
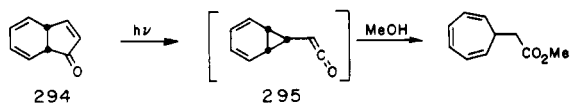
Two acyclic $\alpha,\beta,\beta',\gamma',\delta',\epsilon'$-unsaturated ketones have been investigated, and these species undergo only cis,trans isomerization. Cowan and Baum studied intramolecular energy transfer in **296a** and in the analogous γ,δ-, δ,ϵ-, and ϵ,ζ-unsaturated ketones.[202] Irradiation of **296a** in benzene at 313

296

	R	R'
a:	H	Ph
b:	Me	-CHCH₂
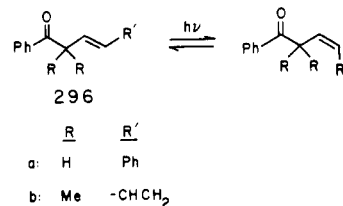
nm gave a photostationary state of the trans and cis compounds, with Φ(trans→cis) = 0.53, the same as the values for the three other compounds studied. The photochemistry of the γ,δ- through ϵ,ζ-unsaturated ketones was interpreted in the following way: absorption of light produces the acetophenone singlet which intersystem crosses and rapidly transfers triplet energy to the styrene chromophore. The situation in **296a** is more complicated since, first of all, the absorption spectrum is not simply a sum of acetophenone and styrene absorptions but has an enhanced nπ* absorption ($\epsilon_{max} \sim 260$ at 330 nm vs. $\epsilon_{max} \sim 40$ at 330 nm for acetophenone). Secondly, Stern–Volmer kinetics indicate that two excited states are responsible for the cis,trans isomerization. One, presumably the styryl ππ* triplet, formed directly from the lowest singlet of the molecule, is unquenchable, while the second, presumably the acetophenone nπ* triplet which has a finite lifetime before energy transfer, is quenchable.[202] Cowan and Baum noted that longer irradiation of **296a** produces an additional compound. This is not surprising in light of Dauben et al.'s observations of many photoproducts from the irradiation of **142**, an analog of **296a** (section II.H.1).

Leermakers and coworkers found similar results with the dienone **296b**.[203] Direct irradiation gave cis,trans isomerization with Φ(trans→cis) = 0.27, while sensitized Φ's of 0.47 and 0.23 were measured with benzophenone and 2-acetonaphthone, respectively. Quenching was not observed, indicating a triplet lifetime of less than 5×10^{-10} sec. The absorption spectrum of **296b** shows a large enhancement of the nπ* absorption, and Leermakers et al. suggested that absorption of light by the acetophenone portion of the molecule is followed by rapid and completely efficient intersystem crossing to the ³nπ* state, from which triplet energy transfer to the diene occurs. The absence of either fluorescence or phosphorescence from **296b** attests to the efficiencies of these processes, as does the failure of quenchers to inhibit the isomerization.[203]

2. 3,5-Cycloheptadienones

3,5-Cycloheptadienones consist of a diene unit which is β at both ends to the carbonyl group. They undergo a variety of reactions, including 1,2-shifts, decarbonylations, and diene electrocyclizations as summarized in boldface in Figure 8. Neither 1,3-shifts nor 1,5-shifts have been observed for these compounds although they could conceivably be undetected intermediates in the decarbonylation reaction.[204] The cyclopentenone or cyclopropanone which would arise from these shifts are, of course, photochemically labile and are potential intermediates in the decarbonylation or they could be "blind-alley", thermally reversible, intermediates. However, no evidence for their formation has been found.

The first report of 3,5-cycloheptadienone photochemistry was by Chapman and coworkers in 1961.[205,206] They reported that the parent compound and the 2-methyl derivative, **297a** and **b**, cleanly decarbonylated upon direct irradiation to form the trienes **298a** and **b**.[205,206]

Seven years later, Schuster and coworkers reported further investigations of the photochemistry of 3,5-cycloheptadienone.[207,208] These workers found that the decarbonylation of **297a** gave a mixture of cis- and trans-**298** upon direct photolysis in Pyrex or quartz in solvents ranging in polarity from hexane to 95% ethanol. The quantum yield for decarbonylation at 313 nm was 0.31.[208] The reaction was not quenched by piperylene (E_T = 59-61) or naphthalene (E = 57). The inefficiency was attributed either to reversible α-cleavage or to radiationless deactivation of the excited singlet. Since the reaction occurred upon 313-nm irradiation, an $n\pi^*$ singlet was involved.[207] Upon sensitized irradiation of **297a** an electrocyclization to the cyclobutene **299** occurs. The conversion to **299** was accomplished by benzophenone (E_T = 68.5), acetone (82), β-acetonaphthone (59), and 1,2,5,6-benzanthracene (52), but not by p-benzoquinone (55) or pyrene (49).[208] In an attempt to determine whether a cis-,trans-3,5-cycloheptadienone was involved as an intermediate in the formation of **299**, Schuster and Blythin carried out sensitized photolyses at low temperatures in the presence of diene trapping agents. Although some quenching by energy transfer (detected by formation of cyclopentadiene dimers) occurred upon irradiation with benzoquinone at dry ice temperature in cyclopentadiene solvent, no Diels-Alder adducts were formed. Furan gave similar negative results. Schuster and Blythin concluded that the cis,trans dienone was not formed, but that the twisted diene triplet cyclized directly to cyclobutene **299**.[208] The quantum yields for the sensitized reaction at 25° by β-acetonaphthone (E_T = 59; Φ_{isc} = 0.84) and fluorene (E_T = 53; Φ_{isc} = 0.93) were 0.54 and 0.01, respectively. A triplet energy of about 54 kcal/mol, exactly that of 1,3-cyclohexadiene, was implicated, leading to the conclusion that a $\pi\pi^*$ triplet was involved in the electrocyclization.[208]

Paquette et al. reported the photochemistry of 2,2,7,7-tetramethylcycloheptadienone (**297c**).[209] By contrast to the parent system, **297c** undergoes the 1,2-shift upon either direct or sensitized irradiation. The quenchers naphthalene or piperylene had no effect on the reaction rate. Paquette suggested that the parent compound undergoes a concerted elimination of CO from a conformation possessing a plane of symmetry (**301**), whereas the tetramethyl compound cannot achieve this conformation due to the severity of nonbonded repulsions between the methyls in such a conformation.[209] It was also suggested that formation of the cyclobutene from the parent compound involved the cis,trans diene, but that this compound could not be formed from the tetramethyl compound for steric reasons.[209]
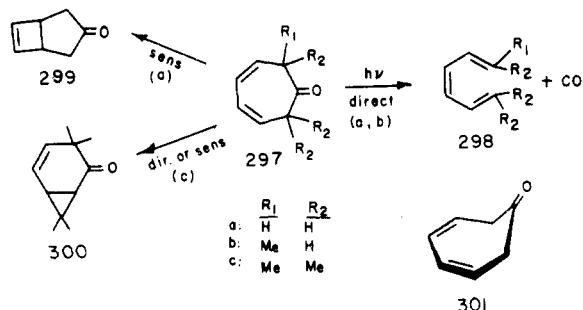
Schuster and Kim, recently reinvestigated the photolysis of the tetramethylcycloheptadienone **297c**.[210] Direct irradiation of **297c** gives both the 1,2-shift product **300** and the decarbonylation product **298c**. In acetone-sensitized photolysis of **297c**, the quantum yield for formation of **300** increases, and no **298c** is formed. Attempted quenching by naphthalene (2 M) failed, but inefficient quenching of the formation of **300** by 1,3-cyclohexadiene ($k_q\tau$ = 0.2 M^{-1}) was observed, and the characteristic cyclohexadiene triplet dimers were formed.

Since the formation of **298c** is not quenched, Schuster concluded that decarbonylation is a singlet reaction, and the 1,2-shift is a triplet reaction, arising from a short-lived triplet of energy near that of cyclohexadiene (53-54 kcal/mol).

Mislow and Gordon reported the decarbonylation of an analog of 3,5-cycloheptadienone, the chiral biphenyl derivative, **302**.[211] Upon direct irradiation of **302**, decarbonylation with retention of configuration and only partial racemization of the starting material occurred in a ratio of about 5:1. The as-

sumed intermediate, **303**, must retain its configuration, and a diradical formulation may perhaps be superior to that shown, since there will be severe torsion about the formal double bond joining the phenyl groups in **303**. Alternatively, the CO could be lost in a stepwise fashion after initial α-cleavage. Mislow noted that **302** racemizes thermally with an E_{act} = 36 kcal/mol, yet absorption of light in the $n\pi^*$ region (300 nm = 95 kcal/mol) results in only a small amount of racemization,[211] demonstrating the fundamental difference between ground-state and excited-state surfaces.
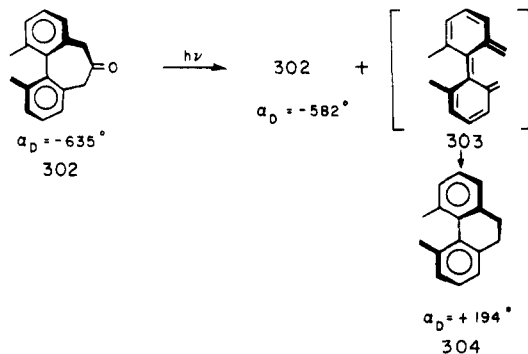
3. 2,7-Bridged 3,5-Cycloheptadienones

The photochemistry of 2,7-bridged 3,5-cycloheptadienones parallels that of the monocyclic systems. The benzo system **305a** undergoes smooth decarbonylation upon direct photolyses in hexane to form **306a**,[212] while sensitized photolysis of **305a** gives the barbaralone **308a**.[213] The photochemistry of the parent bicyclo[4.2.1]nonatrienone has been studied independently by the groups of Mukai,[213] Paquette,[214] and Schechter.[215] All studies revealed the facile decarbonylation of **305b** upon direct irradiation, but Schechter also reported that the cyclobutene **307b** was formed in small amounts ($\sim$3.4%) in the direct irradiation. Schecters' group also reported that small amounts of barbaralone **308b** were formed in the direct photolysis of **305b** at λ >300 nm, but not at 254 nm.[215] All three groups reported that sensitizers ranging in triplet energy from acetone (80 kcal/mol) to Michler's ketone (62 kcal/mol) caused conversion of **305b** to barbaralone **308b**.[213-215] Paquette and coworkers also reported the decarbonylation of **305c** and **305d** upon direct irradiation of **305d**, and the formation of **308d** upon sensitized irradiation of **305d**.[214] These systems are both 3-cyclopentenones and
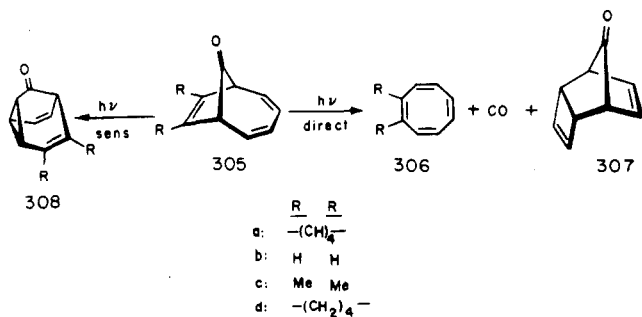
3,5-cycloheptadienones, and the decarbonylation of 305 is analogous to the singlet photochemistry of both of these simpler systems. The triplet reactions of the 305's are oxa-di-π-methane rearrangements involving the 3,5-cycloheptadienone moiety. As with simpler β,γ-unsaturated ketones, intersystem crossing is slower than the singlet reaction. Schuster and Kim recently studied the 7,8-dihydro analog of 305b, bicyclo[4.2.1]nona-2,4-dien-9-one.[210] This compound undergoes decarbonylation ($\Phi^{313nm} = 0.74$) and cyclobutene formation ($\Phi^{313nm} = 0.14$) upon direct irradiation in a variety of solvents and temperatures. Sensitized irradiation gave the 1,2-shift product dihydrobarbaralone; the quantum yield using Michler's ketone is 0.89.[210]

The photochemistry of the bridged 3,5-cycloheptadienones 309a was independently studied by Mukai and coworkers and in our laboratories.[217] Mukai reported that direct photolysis of 6×10^{-3} M solutions of 309a gave the decarbonylation product 310a (25%) and the cyclobutene 311a (15%) along with smaller amounts of a dimer 312a (11%).[216] The structure of

piperylene, or naphthalene.[217] The deuterium labeled analog 309b was also photolyzed to prove that the mechanism involved the usual oxa-di-π-methane bonding changes and not a $[_\sigma2_a + _\pi2_a]$ process.[217] The quantum yields for these reactions have been determined.[218] For direct irradiation in methanol at 254 nm, the quantum yields for disappearance of 309a and for formation of 313a are 0.21 and 0.05, respectively. The 2-acetonaphthone-sensitized formation of 313a has a quantum yield of 0.23, indicating a Φ_{isc} of 0.24 for 309a.[218] A theoretical explanation of these results was provided[217] and will be discussed in later sections.

Rather Rococo versions of this ring system, 315, have also been studied by our group.[120] The photochemistry observed here differs completely from the simple analogs. For the diketone 315a, direct photolysis gives a $[6 + 4]$ cycloreversion, while sensitized photolysis results in a formal $[3,3]$ shift to form 316a.[120] The keto alcohol 315b undergoes a stereospecific "$[3,3]$ shift" to form 316b, indicating that the reaction is intramolecular.

	X	R
a:	-CH$_2$-	H
b:	-CH$_2$-	D
c:	-(CH$_2$)$_2$-	H

	X	A-B
a:	>NCN	-(CH$_2$)$_2$-
b:	>CH$_2$	-CH$_2$CH-
		CH

	X	Y
a:	=O	
b:	H	OH
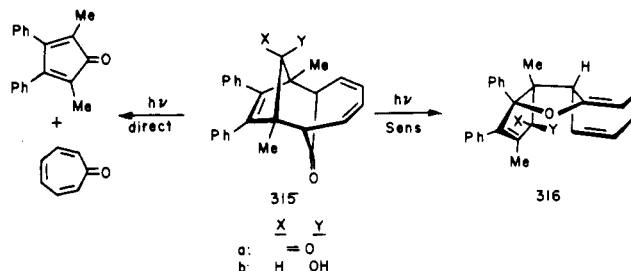
The ultraviolet spectra of the 3,5-cycloheptadienones discussed in this section are given in Table XXIII. All show very intense and structured $n\pi^*$ bands in nonpolar solvents, indicating considerable interaction between the diene and carbonyl systems. Polar solvents broaden the bands and shift the short wavelength bands slightly to longer wavelengths.

the dimer was determined in our laboratories by utilization of LIS reagents.[217,218] Mukai and coworkers found that phenanthrene-, benzophenone-, or fluorenone-sensitized photolyses of 309a in ether gave the dimer 312a in quantitative yield. However, our studies showed that at concentrations of about 10^{-2} M in the presence or absence of sensitizers, dimer 312a was the major product of the photolysis.[217] The formation of dimer could be sensitized by triphenylene and could be quenched by piperylene, oxygen, or cyclohexadiene, but not by naphthalene.[217] Decarbonylation was detected in the presence of quencher.[217,218] Mukai and coworkers found that the cyclohexadiene-tropone 309c adduct exhibited the same type of behavior as the cyclopentadiene-tropone adduct.[216] These results led us to conclude that in nonpolar solvents, decarbonylation and cyclobutene formation involve a singlet excited state, whereas the dimer 312 is formed via a triplet excited state ($E_T = 55-60$ kcal/mol). Intersystem crossing is competitive with singlet reactions. The triplet state is commonly the reactive species in diene dimerizations, and the dienes 314, which are close analogs of 309, undergo dimerization via triplet states to give anti-head-to-head dimers analogous to 312.[219,220] Mukai and coworkers have carried out studies of the conformational processes in 310, which undergoes slow thermal electrocyclization and formation of benzene and cyclopentadiene.[221]

The photochemical behavior of 309 is markedly altered in polar solvents. Direct or sensitized (benzophenone, acetone, or triphenylene) irradiation in polar solvents (acetone, acetonitrile, or methanol) gives the 1,2-shift (oxa-di-π-methane) product 313a. This reaction was not quenched by cyclohexadiene,

4. Barbaralones

This "cross-conjugated" analog, 317, of the compounds discussed in the previous section undergoes decarbonylation upon direct irradiation.[222] The reaction cannot be quenched or sensitized. Photolysis in benzene in the presence of benzophenone gives the novel adduct 318.[223] The analogous decarbonylation of benzobarbaralone has also been observed upon direct irradiation.[224]
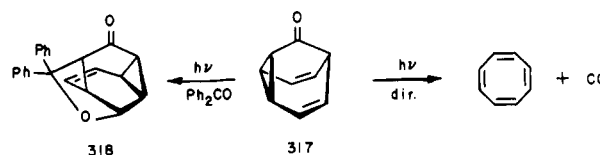
L. β,γ-Unsaturated Aldehydes

The photochemistry of these species has been extensively studied by Schaffner and coworkers.[225-232] Decarbonylation is the most general reaction of β,γ-unsaturated aldehydes, although other reactions occasionally have been observed. Compound 319, which is both a β,γ-unsaturated ketone and a β,γ-unsaturated aldehyde, undergoes photolytic decarbonylation of the aldehyde function to form 320.[225,227] The aldehyde 321a also undergoes decarbonylation, but in this case the isomeric alkenes 322a (95%) and 323a (5%) are isolated.[225,228] Similar results were obtained with 321c.[228] With the corresponding saturated aldehydes, decarbonylation is accompanied by intramolecular hydrogen abstraction resulting in cyclobutanol formation. Irradiation of the deuterated aldehyde 321b gave 322b with all of the deuterium retained,

TABLE XXIII. Ultraviolet Spectra of 3,5-Cycloheptadienones

Compound	λ_{max}, nm (ϵ)	Solvent	Ref
297a	214(5495), 278(602)	EtOH	205
	213, 352.5(5.9), 372.5(4.6)	Et$_2$O	207
	225(6800), sh278(602), 290(567)	95% EtOH	218
297b	217	EtOH	205
297c	235(5170), 282(730)	C$_8$H$_{18}$	209
	243(4680), 290(710)	MeOH	209
302	245(9770), 272(1480), 389.5(760), 297.5(760), 307(575), 317(259)	C$_8$H$_{18}$	211
305a	220(10230), sh262(2700), 270(3550), 277(3240), 320(372)	EtOH	
305b	216(3080), 270(2570), 280(2690), 320(562)	C$_6$H$_{14}$	212
	216(3080), 269(4010), 277(3820), 325(567)	EtOH	215
305c	218(2040), 273(1910), 284(1840), 322(580)	C$_8$H$_{18}$	214
305d	217sh(2590), 273(1410), 283(1380), 318(390)	C$_8$H$_{18}$	214
309	238(2840), 248(3307), 257(4520), 266(4630), 300(480)	MeOH	216
	~215(~5000), 259(4600), 268(5400), 292(460), 303(440), 314(360), 324(150)	C$_6$H$_{12}$	217

319 **320**
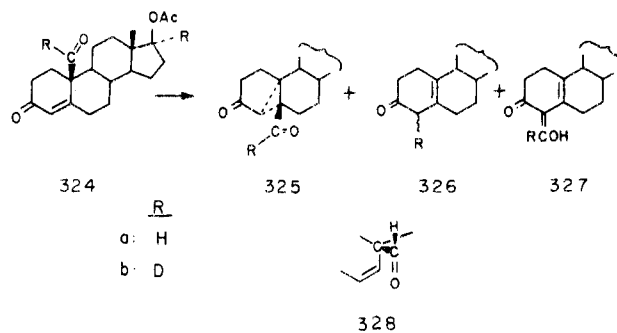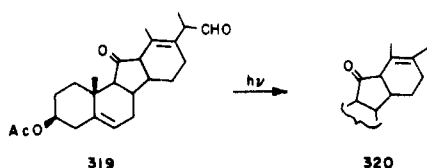
while **323b** contained about 95% of the initial deuterium present in **321b**.[228] When an equimolar mixture of **321b** and **321c** was irradiated, **322b** and **323b** contained all the deuterium (no **322d** or **323d** was formed) indicating that the hydrogen transfer was completely intramolecular. In the corresponding saturated deuterated aldehyde only about 7.5% deuterium is retained.[228] Two mechanisms were considered to explain these results. A concerted decarbonylation was considered unlikely, since reactions of that type typically involve vibrationally excited states in gas-phase decarbonylations of simple ketones. The following mechanism was considered more likely: first, α-cleavage gives a radical pair with some overlap between the π orbitals of the two systems; second, disproportionation of this radical pair occurs faster than diffusion from the solvent cage.[228]

321 **322** **323**

	R$_1$	R$_2$	R$_3$
a:	R	-OCH$_2$CH$_2$O-	
b:	D	-OCH$_2$CH$_2$O-	
c:	H	OH	CH$_3$
d:	D	OH	CH$_3$
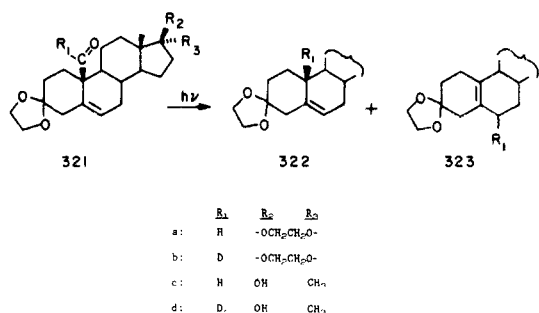
The photochemistry of the γ-formyl-α,β-unsaturated ketone **324** is more complex than that of other β,γ-unsaturated aldehydes. Irradiation of **324a** in a variety of solvents gave the 1,2-shift product **325a** (30%), the decarbonylation product **326** (15%), and a tautomer **327** (25%), of the 1,3-shift product.[226] When a mixture of **324a** and the dideuterio derivative **324b** was photolyzed, the following observations were made: deuteration slowed down the disappearance of **324**, and the rates of formation of **326** and **327** were both decreased; the 1,2-shift product was formed faster in the deuterated than in the nondeuterated material. The formation of all three products was sensitized by acetophenone, and low-temperature emission studies indicated that **324a** has a low-

324 **325** **326** **327**

R

a: H

b: D

328

est energy triplet (0–0 band ~400 nm, τ = 28 msec) nearly identical with that of the analog where the aldehyde function is replaced by a methyl (0–0 band ~400 nm, τ = 30 msec).[231] This implies that all three products are formed from a triplet state, probably $\pi\pi^*$ in character, which is the lowest triplet state of the molecule. At 71°K, the formation of **327** is eliminated.[231] Circular dichroism studies led to the conclusion that **328** is the most favored conformation of **324**. The deuterium isotope effects indicate that two different primary processes occur: a 1,2-shift, which shows an inverse isotope effect compatible with initial carbonyl carbon–β-carbon bonding, and α-cleavage which shows a normal isotope effect. The latter gives a caged radical pair, which can recombine to form **327** or disproportionate to form **326**. The latter is favored at higher temperature.[231]

A second γ-formyl-α,β-unsaturated ketone, **329**, has been studied by these workers. The major product of photolysis is the decarbonylated product **330**.[229]

329 **330**
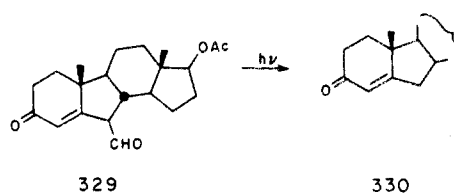
The study of optically active and isotopically labeled laurolenal revealed further subtleties. In an earlier section, the methyl ketone **331** (R = X = Me) was discussed. Direct photolysis gave predominantly the 1,3-shift product while sensitized photolysis gave the 1,2-shift product. With the aldehyde (*R*)-(+)-laurolenal (**331a**), decarbonylation is the sole process observed.[225,230] The product was partially racemized, and the extent of racemization indicated that **332a** and **333a** were formed in a ratio of 89.5:10.5.[225,230] Recovered **331** retained

331   332   333

	R	X
a:	Me	H
b:	Me	D
c:	CD₃	H
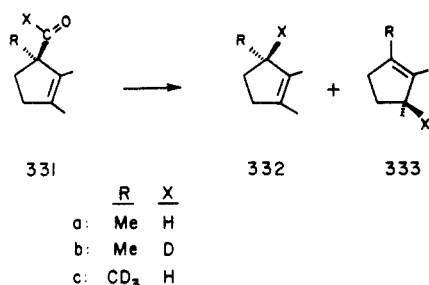
its optical purity, indicating that no 1,3-shifts occurred. This ratio of **332** to **333** was not subject to a deuterium isotope effect. Thus, **331b** gave the products with complete retention of deuterium and with the same degree of racemization as observed with the undeuterated material. Even in the presence of *n*-Bu₃SnH, no deuterium was lost.[230] Photolysis of the racemic trideuterio compound **331c** gave **332c** and **333c** in an 88.7:11.3 ratio.[232] Quantum yields for disappearance of **331** were as follows: Φ^{313}_{hexane} = 0.61; Φ^{297}_{hexane} = 0.54; $\Phi^{313}_{C_6H_6}$ = 0.39; $\Phi^{297}_{C_6H_6}$ = 0.32; $\Phi^{313}_{t\text{-BuOH}}$ = 0.44; $\Phi^{297}_{t\text{-BuOH}}$ = 0.43.[232] Neither sensitization nor quenching of the reactions of **331** could be effected. However, photolysis in acetone did lead to consumption of **331** without formation of decarbonylated products. Schaffner and coworkers suggest that a singlet excited state of **331** is involved in the decarbonylation.[232]

β,γ-Unsaturated aldehyde **334**, an exocyclic analog of laurolenal, undergoes photolytic decarbonylation exclusively, and the products **335** (70%) and **336** (30%) contain 100 and 90% of the original deuterium, respectively.[232] In the pres-

334   335   336
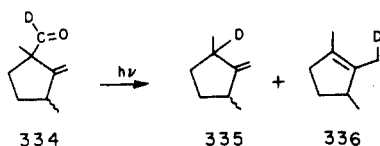
ence of tri-*n*-butyltin hydride, the two products are formed in the same ratio with 100 and 78% deuterium, respectively, along with the alcohol corresponding to **334**.[232] For laurolenal and **334**, Schaffner and coworkers proposed that the primary photochemical process was α-cleavage of excited states of the rotamers **337** and **339** to give different radical pairs **338** and **340**, respectively.[232] The formulation of **338** and **340** differs from the unusual valence-bond picture of a singlet nπ* state of an aldehyde mainly in the stretching of the C_{CO}–C_α bond. After formation of the radical pairs, cage recombination, leading to quantum inefficiency, can occur, or decarbonylation by hydrogen transfer can occur. The radical pair **338** will give only the "unshifted" decarbonylation product, while **340** will give both "unshifted" and "shifted" decarbonylation products.[232] The solvent and wavelength dependences which were observed were attributed both to differences in rotamer populations, and to the wavelengths of absorption of rotamers **337** and **339**.[232]

337   338

339   340
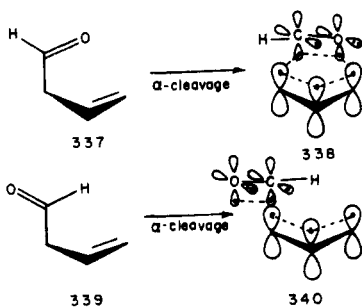
Dürr and coworkers have investigated the β,γ-unsaturated aldehydes **341a-d**. These species undergo decarbonylation and concomitant oxidative cyclization.[233] Presumably, forma-

341   342   343

	Ar	R
a:	Ph-	H
b:	p-MeOPh-	H
c:	p-ClPh-	H
d:	Ph-	D
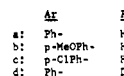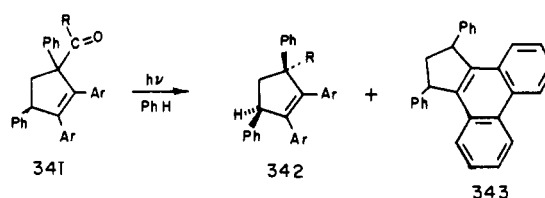
tion of **343** is the result of the well-documented singlet cyclization of the *cis*-stilbene moiety. Photolysis of the deuterated aldehyde **341d** gave complete retention of the deuterium, indicating the intramolecular nature of the reaction. The decarbonylation can be sensitized by acetophenone,[233] indicating a triplet state for the decarbonylation, in contrast to the compounds studied by Schaffner. The quantum yield for formation of **342a** is 0.23 in benzene.[234] Pratt recently reported that the decarbonylation of 2,2-dimethyl-4,4-diphenylbut-3-enal was accompanied by a small amount of the 1,3-(formyl) shift product.[98]

Schaffner and coworkers have studied the cyclohexene-carboxaldehyde **344**, which undergoes photolytic decarbonylation with formation of a single isomer, **345**.[232] The aldehyde deuterium is lost to the extent of 9% in pentane, and to the extent of 20% in the presence of tri-*n*-butyltin hydride. The quantum yield is wavelength dependent in hexane (Φ^{313} = 0.55; Φ^{297} = 0.42) but not in *t*-BuOH (Φ = 0.44).[232]

344   345
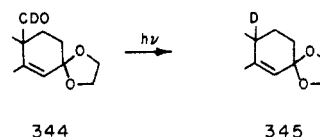
In all of the previous cases cited, rapid cleavage to form the radical pair should be facilitated by the formation of the stabilized allylic radical. In agreement with this, the 7-methylenenorbornane-1-carboxaldehyde (**346**), which, for geometrical reasons, cannot give a resonance-stabilized allylic radical, does not undergo decarbonylation or other reactions characteristic of α-cleavage. Irradiation of **346** in 2-propanol gives only the photoreduction product **347** in a reaction probably involving the nπ* triplet, since piperylene efficiently quenches the reduction.[232] In pentane, products resulting from α-cleavage of H, **348** (R = Me) (10 parts) and **348** (R = Et) (6 parts), and the reduce product **347** (100 parts) are formed, along with other products in a complex mixture.[232] This result suggests that the α-cleavage reaction of β,γ-unsaturated aldehydes from which the stabilized allylic radical can be formed is faster than intersystem crossing, but that intersystem crossing occurs at the usual rate for aldehydes (~10^9 sec⁻¹).

348   346   347
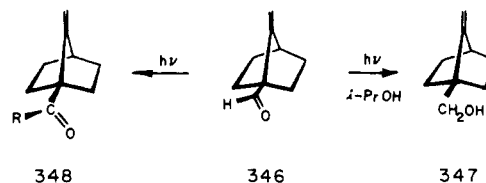
The ultraviolet spectra of representative β,γ-unsaturated aldehydes are given in Table XXIV. It is notable that only **346**, which does not undergo α-cleavage of the carbon–carbon bond does not have an enhanced nπ* absorption. Whether

TABLE XXIV. Ultraviolet Spectra of β,γ-Unsaturated Aldehydes

Compd	$\pi\pi^*$	λ_{max}, nm (ϵ)	Solvent	Ref
321a	226(1255)	310(113)	EtOH	232
324a	246(15600)	314(320)	EtOH	226
331a	228(1630)	305(135)	EtOH	232
		305(132)	C_8H_{18}	232
334a		296.5(71)	EtOH	232
		299(62)	C_8H_{18}	232
344		308(103)	EtOH	232
		302(118)	C_8H_{18}	232
346		298(10)	EtOH	232
		302(24)	C_8H_{18}	232

the latter is the source of, or only coincidentally related to, the failure of this compound to α-cleave is discussed in the later sections of this review.

Several facets of the β,γ-unsaturated aldehyde work are of particular interest upon comparison to β,γ-unsaturated ketone photochemistry. First, the decarbonylation reaction seems without doubt to involve initial α-cleavage, and yet the reaction is nearly completely intramolecular. Second, the favored conformation, **328**, postulated for β,γ-unsaturated aldehydes, is precisely that required to explain the stereochemistry of the stereoselective oxa-di-π-methane reaction of **95** cited earlier.

M. Enol Esters

The photochemical 1,3-shifts of aryl esters (photo-Fries reactions) were known well before those of enol esters but will be discussed later. The photochemistry of enol esters, aryl esters, and the related enamides has been reviewed recently.[235-237] The most general reactions of the enol ester species **349** are 1,3-acyl shifts to give β-diketones **350**, isolated as the enol tautomers. For nonenolizable β-diketones the reaction is often photochemically reversible, as shown in the next section, while β-diketones which are largely enolic in solution provide excellent filters and make the 1,3-shift of **349** to **350** proceed only to low conversions.[237]

longed irradiation in transparent solvents produces decarbonylation with formation of acetophenone.[238]

Gorodetsky and Mazur investigated the photochemistry of a variety of acyclic, cyclic, and steroidal enol benzoates, **349-Ph-b–e** and acetates, **349-Me-b–h** .[239-242] In most of the cases, direct irradiation gave a 1,3-acyl shift with formation of the enol form of the β-diketone product **350**. Exceptions to this behavior were observed with the compound **349f**, which formed the 1,3-shift product **350f** (17%) and the products of α-cleavage followed by hydrogen abstraction, **351** (5%), or dimerization, **352** (7%).[242] The related 1-(2-methylcyclohexenyl) acetate (**349h**) gives only 2% of the 1,3-shift product, along with a number of α-cleavage products related to **351** and **352**.[240] When an equimolar mixture of **349g** and **349g-d_6** containing fully deterated acetate methyls was photolyzed, only d_0 and d_6 1,3-shift products were formed, indicating that the 1,3-shift was wholly intramolecular.[240]

An exception to the low conversions commonly observed in these reactions is observed with **349I**, which is a γ-keto-β,γ-unsaturated ester. This compound undergoes the 1,3-shift to **350I** in 60% conversion.[243] This compound has a lowest singlet of the $n\pi^*$ type,[243] whereas most of the other enol esters undergo rearrangement upon irradiation into the $\pi\pi^*$ band.[237] An exception is the ester **349I**, which is stable upon irradiation into either the $\pi\pi^*$ or $n\pi^*$ bands.[244] This compound has a lowest $\pi\pi^*$ triplet.[245]

As with the corresponding $\beta,\gamma,\delta,\epsilon$-unsaturated ketones, dienyl esters undergo both 1,3- and 1,5-shifts. With **353a**, 29% of two enol forms of **354a** was formed by a 1,3-shift, and 6.6% of the 1,5 shift product **355a** was formed.[241] Loss of acetyl was also observed in 4% yield. The methyl derivative **353b** gave 17% of the 1,3-shift product, **354b**, and 13% of the 1,5-shift product, **355b**. However, the phenylalkenyl

	R
a:	H
b:	Me

enol esters **349j** and **k**, which could undergo vinylogous photo-Fries reactions (1,5-shifts), undergo only 1,3-shifts accompanied by small amounts of α-cleavage reactions.[246]

Irradiation of enol lactones gives somewhat different behavior. Thus, steroidal lactone **356a** gives both 1,3-shift and decarbonylation products, **357** and **358**, respectively,[247] while the bicyclic lactone **356b** gives the product resulting from trapping of a ketoketene intermediate.[248] The monocyclic

A simple example of the photochemical 1,3-shift is provided by the conversion of vinylbenzoate **349a** to benzoylacetaldehyde **350a** in 6% conversion in benzene solution.[238] Pro-

TABLE XXV. Ultraviolet Spectra of Enol Esters

Compd	λ_{max}, nm (ϵ)	Solvent	Ref
353b	238(20500)	C_6H_{12}	241

lactone **356c** undergoes both retro-Diels–Alder and decarbonylation reactions,[247] while **356d** and **e** give only retro-Diels–Alder reactions on photolysis.[250] In these last two cases, triplet-sensitized photolysis gave different products (unidentified), implying that the retro-Diels–Alder reaction is a singlet reaction.[250] All of these reactions could occur from a diradical formed by acyl–oxygen cleavage in the excited state.

The δ-enol lactone **360** undergoes decarbonylation at 77 K,[251] a reaction reminiscent of those of 3-cyclopentenones.

360
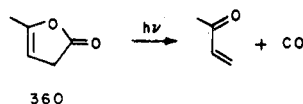
By contrast, the vinylidene carbonates do not decarbonylate, but undergo reactions characteristic of alkene triplets. Compound **361a** undergoes both photoreduction of the double bond and dimer formation upon benzene-sensitized irradiation in 2-propanol. In the absence of a hydrogen donor, **361a** gives **363a** upon acetone-sensitized photolysis.[252]

363 361 362

```
R        R
a:  ⁿPr     ⁿPr
b:  -(CH₂)₄-
c:  -(CH₂)₆-
d:  -(CH₂)ₙ- [n= 8]
e:  -(CH₂)₁₀-[n=10]
```
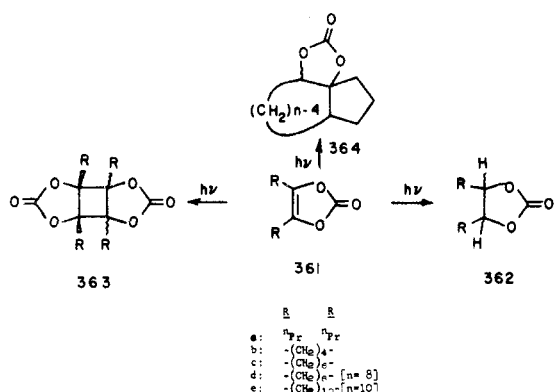
The cyclohexene derivation **361b** gives only photoreduction, while **361c** gives only dimer on irradiation even in the presence of 2-propanol.[252] The medium ring compounds **361d** and **e** are converted to the products of intramolecular hydrogen abstraction–radical recombination, **364d** and **e**, upon acetone-sensitized photolysis.[252]

Finally, the phthalide **365** has been found to undergo a 1,3-shift, and the composition of the photostationary state can be markedly affected by the wavelength of irradiation.[253] Thus, the ratio of phthalide **365** to indanone **366** changes from 100:0 at λ 355 nm to 50:50 at λ 285 nm.

365 366
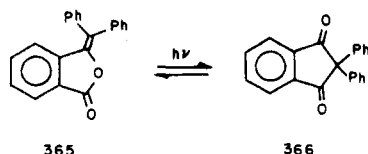
Similar 1,3-shifts have been observed with alkenylamides.[235,237,254] The ultraviolet spectra of a relevant enol ester is given in Table XXV. The $n\pi^*$ transition in vinyl esters is usually not seen in the near-uv, and the $\pi\pi^*$ absorption of the vinyl moiety is shifted only slightly by the acetoxy function.

N. β-Diketones

The reactions of some of these species have been discussed in the previous section. Most β-diketones with one or

two hydrogens α to both carbonyls are enolic and do not undergo photoreactions. However, nonenolizable β-diketones readily undergo 1,3-shifts and other reactions such as decarbonylation.

In a reaction cited in the previous section, prolonged irradiation of benzoylacetaldehyde, results in formation of acetophenone and CO,[238] while **349-Ph-e**, the product of a 1,3-shift of 1-cyclohexenyl benzoate, undergoes a photochemical type II reaction to form **367** in 72% yield.[239]

349-Ph-e 367
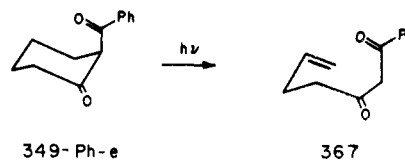
Nozaki et al. found that the 2,2-dimethyl-1,3-cyclohexanediones **368a** and **b** underwent 1,3-shifts upon irradiation in benzene.[250] The dimethyl compound **368a** gave **369a** in 70% yield, while the tetramethyl compound **368b** gave a pseudo-photostationary state consisting of **368b**, **369b** and the endocyclic isomer **370b**, in a 3:95:2 ratio. Longer irradiation in

368 369 370

```
     R    R₁
a:   H    Me
b    Me   Me
c:   H   -(CH₂)₄
```
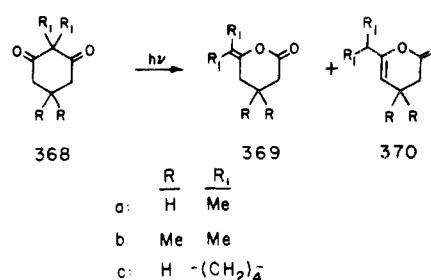
benzene gave expulsion of ketene from **370b** (see previous section).[251] The 1,3-shift of **368b** had been observed earlier by Cookson and coworkers.[249] The reaction of **368b** was considered by Nozaki et al. to be a triplet reaction due to their observations of quenching by piperylene and sensitization by benzene (E_T = 85). Propyl bromide enhances the reaction rate, indicating a heavy-atom acceleration of intersystem crossing to the reactive triplet state. Schaffner and coworkers observed only the 1,3-shift upon irradiation of **369c**.[255]

Different results are obtained when the two carbonyls are not contained in the same ring. Thus 3,3-dimethylacetylacetone (**371a**) undergoes α-cleavage to form biacetyl (3%) and **372a** (33%) along with the 1,3-shift product **373** (20%).[250]

371 372 373 374

```
     R₁   R₂
a:   Me   Me
b:  -(CH₂)₄-
```
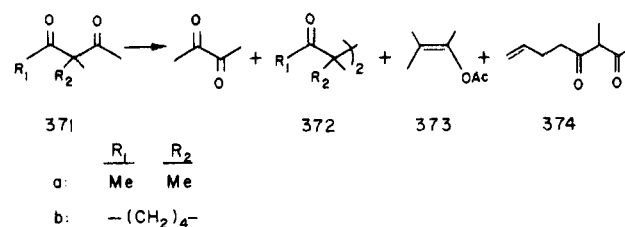
The authors suggest that α-cleavage followed by in-cage (**373**) and out-of-cage reactions occur. The acetylmethylcyclohexanone (**371b**) gives a trace of biacetyl, 6% of 2-methylcyclohexanone, and 14% of the type II photoproduct **374**, along with 35% recovered **371b**.[251] The spiro system, **371c**, gives only the 1,3-shift product arising from migration of the
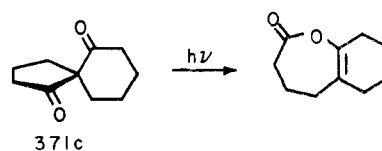
371c

five-membered ring carbonyl.[255] This reaction occurs upon either direct or acetophenone-sensitized irradiation, and is accompanied by a faster photoracemization of **371c** when optically active reactant is used. The results are compatible with α-cleavage of the cyclopentanone from the triplet state, and perhaps from the singlet state also.[255]

Krapcho and Waller have studied the decarbonylation of 1,3,5-cyclohexanetriones as a route to multispiro compounds.[256] Cookson and coworkers previously reported concomitant 1,3-shift and decarbonylation reactions upon photolysis of hexamethyl-1,3,5-cyclohexanetrione.[249] Krapcho and Waller found that a large number of compounds represented by the general formula **375** undergo both decarbonylations and 1,3-shifts. The resulting β-diketones **376** also undergo both of these reactions. A similar reaction had been reported
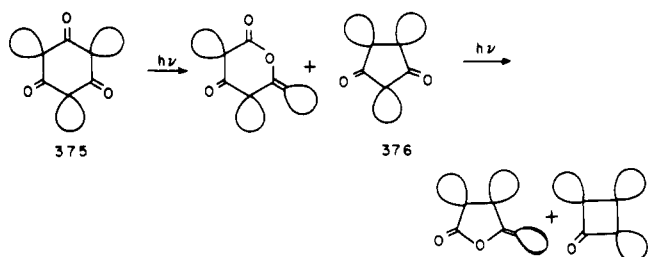
earlier but not studied in detail.[257] Krapcho and Waller found that sensitizers usually had no effect on the reaction and that the ease of decarbonylation relative to 1,3-shift was in the order $C_7 > C_5 > C_6 \gg C_4$ for the various spirocyclic ring sizes. They concluded that diradical intermediates (α-cleavage) were involved and that the least stable ones (C_4) cyclized rapidly to 1,3-shift products before decarbonylation, while the more stable decarbonylated before cyclization.[256] A diradical or concerted mechanism from an $n\pi^*$ triplet state had been proposed earlier.[249]

The study of 1,3-cyclobutanediones as a source of cyclopropanones has been carried out by several groups.[258] Cookson and coworkers observed a 1,3-shift in low yield upon photolysis of **377**,[249] while Turro et al. found that tetramethyl-1,3-cyclobutanedione gives tetramethylcyclopropanone along with dimethylketene, tetramethylethylene, and the 1,3-shift product **378a** in low yields.[258] The intermediacy of the oxallyl
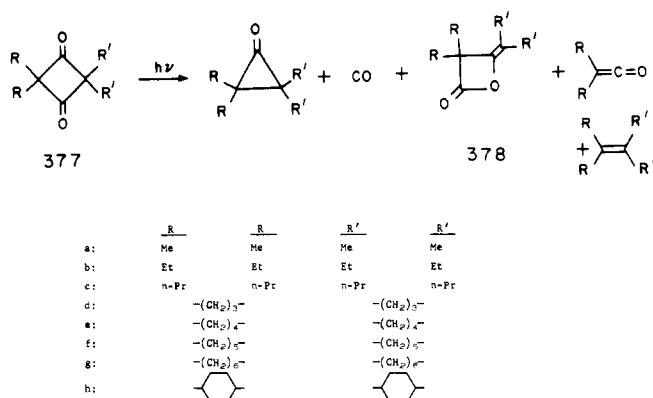
zwitterion (diradical?) in the formation of the cyclopropanone is probable. The chemistry of cyclopropanone formed in this way has been the subject of several studies.[259] Other tetraalkyl derivatives, **377b** and **377c**, are also found to give the corresponding alkenes, **378**, upon photolysis.[260] Several groups have studied the corresponding dispiro compounds **377d-h**.[259,261-263] The photochemistry of these species is quite solvent dependent, and many products are formed. The two principal processes are, however, ketene formation and decarbonylation to form cyclopropanones, which undergo

TABLE XXVI. Ultraviolet Spectra of β-Diketones

| Compound	λ_{max}, nm (ϵ)	Solvent	Ref
371c	310(108)	C_5H_{12}	255
	299(80)	EtOH	255
375 ($n = 4$)	244(218), 303(162)	MeOH	256
($n = 5$)	224(535), 291(135)	MeOH	256
($n = 6$)	230(467), 295(128)	MeOH	256
($n = 7$)	235(281), 300(85)	MeOH	256
379a	281(102)	EtOH	264
382a	290(65)	EtOH	265
	296(65)	C_6H_4	265
382b	292(50)	EtOH	265
	296(52)	C_6H_{12}	265
2,2,5-Trimethyl-1,3-cycloheptanedione	sh270(741), 290(42)	EtOH	62
	294(35)	C_6H_{14}	62
Spiro[4.4]nonane-2,6-dione	302(126)		a

a D. A. Lightner, G. D. Christiansen, and J. L. Melquist, *Tetrahedron Lett.*, 2045 (1972).

subsequent thermal and photochemical reactions. Only in the case of **377d** was a 1,3-shift product, **378d**, isolated.[259] In inert solvents, the alkene is generally the major product,[259,261,262] while in methanol the cyclopropanone dimethyl ketal is formed and reacts with solvent or oxygen.[259,263]

Nozaki and coworkers have studied several bicyclic nonenolizable β-diketones.[264,265] They found that **379a** and **b** gave the 1,3-shift products **380 a** and **b**, in 98 and 83% yield, respectively.[264] By contrast, **381** gave only products of cyclo-

propyl rupture upon photolysis. Compound **382a** gave two of the possible 1,3-shift products, **383a** (43%), and **384** (1.5%), along with the products of decarbonylation, **385** (5.6%), and subsequent rearrangement, **385'** (8%).[265] The rate of formation of the 1,3-shift products was drastically curtailed when the irradiation of **382a** was carried out in the presence of piperylene, suggesting that an $n\pi^*$ triplet state is responsible for these reactions.[265] The [3.2.1] system **382b** undergoes only the 1,3-shift to **383b**.[265] These reactions are all suggested to proceed via α-cleavage from the $n\pi^*$ triplet state.[265]
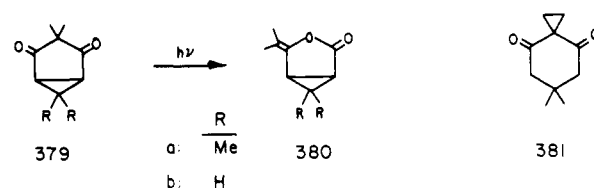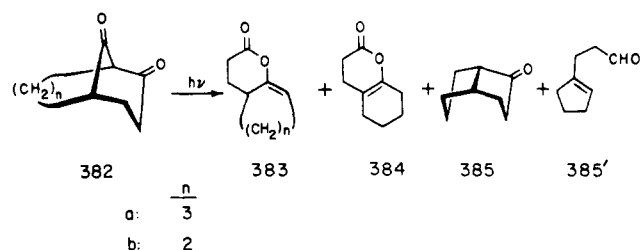
All the photochemical reactions of β-diketones discussed so far, like those of enol esters,[235-237] can be rationalized on the basis of diradical intermediates, formed by α-cleavage from $n\pi^*$ excited states. The yields of 1,3-shift products are quite high in cyclic cases, but drop drastically in the acyclic cases studied.

The α-cleavage in β-diketones has been postulated to involve triplet states in many cases, in contrast to the β,γ-unsaturated ketones and aldehydes. However, with the β-diketones, the lowest triplet state should be an $n\pi^*$ state, and such states are known to α-cleave faster than the corre-

sponding singlets. By contrast, β,γ-unsaturated ketones, whose lowest triplet states are probably $\pi\pi^*$ states, undergo the oxa-di-π-methane rearrangement. With β-diketones, the oxa-di-π-methane rearrangements, which would produce acyloxiranes, are not observed.

An interesting photochemical conversion of enols to β-diketones or β-keto esters, and vice versa, has recently been reported by several groups.[266] Irradiations of the highly enolic species give high concentrations of the β-dicarbonyl systems, which absorb much less strongly. Reversion to the enol form occurs to some extent photochemically as well as in a dark reaction.

The ultraviolet spectra of some β-diketones are given in Table XXVI. As with other β,γ-unsaturated carbonyls, enhanced $n\pi^*$ absorptions are observed. The spiro[4.4]nonane-2,6-dione spectrum is particularly revealing, since the $n\pi^*$ maximum is about three times more intense than twice that of the monoketone.[267]

O. α-Aryl Carbonyl Compounds

1. α-Aryl Ketones

a. Nonconjugated

Quinkert et al. discovered the facile photochemical decarbonylation of α-phenyl ketones. The acyclic benzyl ketones 386a–c undergo decarbonylation in solution upon direct irradiation to form the radical coupling products, 387–389.[268] Irradiation of either 386c or an equimolar mixture of 386a and 386b resulted in the formation of a statistical ratio of the three possible radical coupling products, 387–389, indicating the formation of free, as opposed to caged, benzylic radicals in solution.[268]

The dibenzyl ketone system has been subjected to close scrutiny by two groups. Engel found that dibenzyl ketone (386a) undergoes decarbonylation in benzene at 313 nm with a quantum yield of 0.7, and that the only products were CO and diphenylethane.[269] The reaction was not sensitized by xanthone ($E_T = 74$), nor did 386a quench the photoreactions of butyrophenone ($E_T = 75$) or acetophenone ($E_T = 74$). Decarbonylation of 386a was sensitized with acetone ($E_T = 80$). The weak 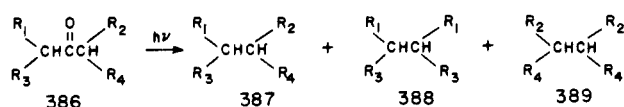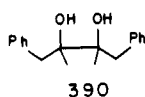fluorescence of dibenzyl ketone ($\Phi_f = 0.04$; $\tau_s = 3.61$ nsec) was quenched by piperylene ($k_q = 5.9 \times 10^7$), 1,3-cyclohexadiene (4.7×10^8), and di-tert-butylnitroxide (5.9×10^9). In the quenching studies, the disappearance of ketone was hardly affected, indicating that the triplet lifetime of 386a was on the order of 10^{-10} sec. The quenching observed was attributed entirely to singlet state quenching. The very short triplet lifetime was thought to be due to rapid α-cleavage of the excited triplet.

Robbins and Eastman carried out parallel studies of substituted dibenzyl ketones.[270] These workers also concluded that a very short-lived triplet was responsible for the α-cleavage reaction.[270] Benzonitrile, which has a higher singlet energy than dibenzyl ketone but has a lower triplet energy ($E_T = 77$), quenched the formation of CO from 386a. Quantum yields for the decarbonylation of substituted dibenzyl ketones were as

follows: $\Phi(-CO) = 0.70$ for 386a; 0.71 for 386d; 0.66 for 386e; 0.65 for 386f; <0.02 for 386g.[270] Dibenzyl ketone and its p-methoxy derivatives decarbonylate, while the p-cyano derivative is unreactive. The excited singlet energy of benzonitrile is higher than that of simple ketones, so that the lowest singlet energies of 386a and 386d–g should all be similar. However, the lowest triplet excitation in 386g is "localized" in the benzonitrile moiety, rendering it unreactive toward α-cleavage.[270]

Robbins and Eastman found that the ratio of bibenzyls formed from 386e was statistical and independent of solvent viscosity. Thus, diffusion of the acyl-benzyl radical pair out of the solvent cage probably precedes the second α-cleavage, or else nonstatistical in-cage coupling products would be anticipated. Indeed, acyl radicals were trapped by 2,2,6,6-tetramethylpiperidine-N-oxyl.[271] However, since the acyl radical cannot be trapped by tri-n-butyltin hydride, the rate of the second α-cleavage must be about 10^8 sec^{-1} for acyl radicals.[271]

The photochemistry of benzyl methyl ketone (386h) differs markedly from that of the dibenzyl ketones. Thus, 386h gives p-methylacetophenone (0.4%), the pinacol, 390 (11.2%), and bibenzyl (387a) upon irradiation in hexane.[272] The ratio of bibenzyl to p-methylacetophenone decreases with increasing concentration of 386h. In tert-butyl alcohol, pinacol formation is suppressed but o-methylacetophenone is formed also. A mechanism involving α-cleavage, in-cage formation of acetophenones, and diffusion out of cage with subsequent bibenzyl formation is probable.

In cyclic systems, the diradical formed by α-cleavage abstracts a hydrogen intramolecularly before decarbonylation as shown by the behavior of 391[18] and 392a and b.[273] The latter reaction proceeds to give mainly the trans aldehyde 394, at low conversions, and can be carried out in benzene or methanol, indicating the lack of competing ketene formation.[273]
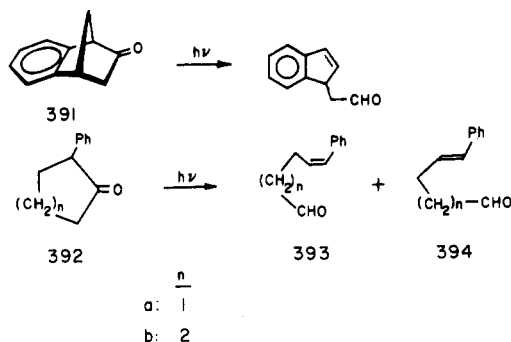
The related bicyclic α-phenyl ketones 395a and b undergo decarbonylation, followed by intramolecular hydrogen abstraction.[274] The difference between these compounds and the related compounds 391 and 392 doubtless arises both from the fact that the latter would give primary radicals upon loss of CO and because there is no steric difficulty in intramolecular hydrogen abstraction by the acyl radical, whereas the acyl radical formed from 395a has no hydrogen to abstract, and in the case of 395b could do so only with difficulty. Furthermore, loss of CO from 395a or b gives relatively stable tertiary radicals.
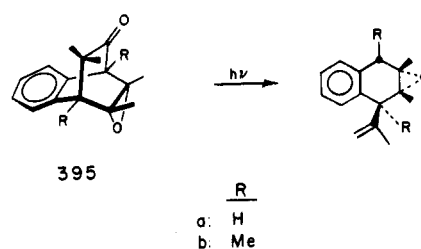
Givens and coworkers have studied a number of phenylacetates which are analogous to the benzyl ketones. Detailed studies of the cis- and trans-diphenyl lactones 396,[275] as well as of acyclic diaryl esters 397,[275,276] indicate that decarbonylation occurs from a triplet which can be sensitized and quenched, and that diradicals (from 396) or free radicals (from 397) are intermediates in these reactions. Quantum
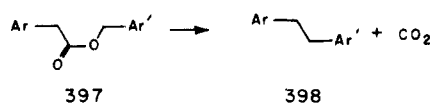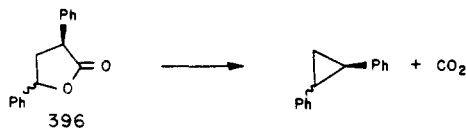
yields for these reactions varied from 0.03 to 0.25 in various cases. With the unsymmetrical diaryl compounds 397 (Ar = p-MeOPh; Ar' = p-MePh) the ratio of bibenzyls formed was slightly solvent dependent, and about twice the amount of unsymmetrical bibenzyl expected from statistical considerations is formed. A cage effect is invoked to explain these results.[275] With α- and β-naphthylmethyl phenylacetates 397 (Ar = Ph; Ar' = α- or β-naphthyl), the unsymmetrical biaryls are formed in much larger than statistical amounts, indicating a large cage effect.[276] In these cases, the reactions could not be sensitized or quenched, indicating the involvement of singlet excited states in α-cleavage.

The polycyclic dibenzyl ketone 399 undergoes loss of ketene upon direct photolysis.[277] The reaction probably proceeds by initial α-cleavage.
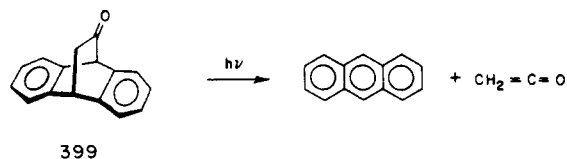
b. 2-Indanones

2-Indanones (400), which are benzologs of 3-cyclopentenones, undergo facile photodecarbonylation to form o-quinodimethanes, and the latter generally undergo subsequent photochemical or thermal reactions. Quinkert and coworkers
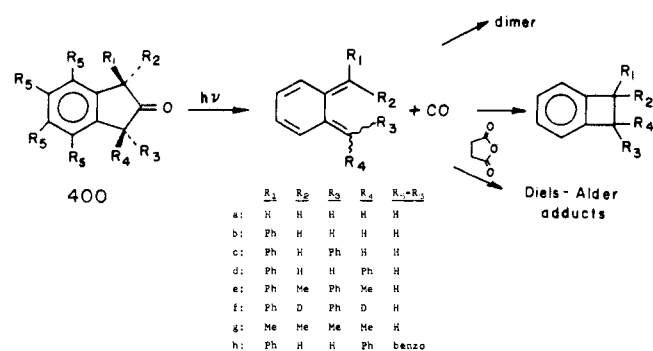
found that 400a–c undergo decarbonylation with formation of dibenzocyclooctane dimers, benzocyclobutanes, or, in the presence of maleic anhydride, Diels–Alder adducts.[268] Recent flash photolysis studies of the stereochemistry of decarbonylation of 400c and 400d at low temperatures reveal a lack of stereospecificity in the decarbonylation and implicate

diradical intermediates in these reactions. Similar results are obtained with cis and trans isomers of 400e and f.[278] These reactions are unquenchable, and singlet excited states are postulated precursors of α-cleavage.[278] In the crystalline phase, the decarbonylations of cis and trans isomers of 400e and f with formations of benzocyclobutanes are highly stereospecific: cis-2-indanones give cis-benzocyclobutanes, and trans give trans.[279] Biradical intermediates which are unable to undergo random rotations about single bonds can explain these results.

Starr and Eastman studied the tetramethyl-2-indanone 400g. In this case, a rapid 1,5-hydrogen shift produces 401 as the only product.[121] These workers also found that 400a gives mainly the ketone reduction product upon irradiation in cyclohexane.[121] The phenanthrene derivative 400h undergoes decarbonylation with formation of the trans-diphenylphenanthrenocyclobutane.[280]
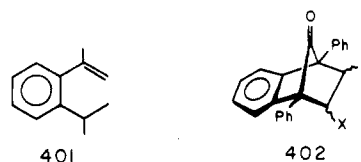
A number of benzonorbornenones, represented by the general formula 402, undergo facile photodecarbonylations, and the resulting o-quinodimethanes undergo subsequent thermal ring openings or 1,5-shifts to restore the benzene ring.[281] A related cyclopentadienone [4 + 4] dimer decarbonylates and subsequently cyclizes to a cyclobutane.[282]

c. α,β-Unsaturated-α-aryl Ketones

These species generally undergo α-cleavage and subsequent radical reactions upon photolysis. The most recent evidence for this comes from CIDNP studies of the photolysis of diphenylacetophenone (403).[283] Muller and Closs irradiated 403 and observed CIDNP in the starting material. The nature of the signals indicated that recombination occurred from the triplet radical pair 404. The CIDNP signals were quenched by piperylene, indicating that a triplet excited state of 403 was responsible for the α-cleavage.[283] Heine has carried out a number of studies of the photochemistry of benzylphenyl ketones.[284-286] In the cases of the fully arylated compounds
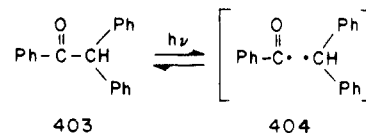
405a, both α-cleavage products and the products of 1,3-shift of an aryl group, 406, were formed.[284] With 405b–d, the rates of α-cleavage to form benzaldehyde and the coupling products 407 were measured in order to probe the effect of α-substitution on α-cleavage reaction rates. By measuring the rate of quenching by naphthalene, the rates of a α-cleavage were found to be 8×10^6, 9×10^7, and 1.7×10^8 sec^{-1} for 405b, 405c, and 405d, respectively.[285]
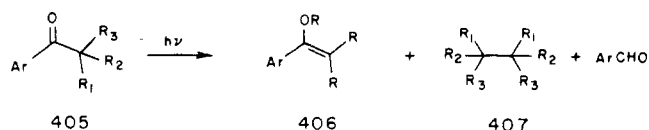
For a series of benzoin derivatives, **405e**, α-cleavage was found not to be quenched by naphthalene or piperylene. In these cases, either a very short-lived triplet ($\tau < 2 \times 10^{-10}$ sec) or α-cleavage before intersystem crossing was postulated. The occurrence of α-cleavage in benzoin and benzoin ethers has been proven by CIDNP experiments,[287] as well as by trapping of both radical fragments by 2-nitroso-2-methylbutane.[288] More recently, Pappas and Chattopadhyay have studied the isopropyl benzoin ether, **408**.[289] At low conver-

$$\underset{\textbf{408}}{\overset{\text{O O}^{i}\text{Pr}}{\underset{\text{PhCCHPh}}{\parallel \; |}}} \longrightarrow \underset{\textbf{409}}{\overset{\text{O O}}{\underset{\text{PhCCPh}}{\parallel \; \parallel}}} + \overset{^{i}\text{PrO O}^{i}\text{Pr}}{\underset{\text{Ph CH CH Ph}}{| \qquad |}}$$
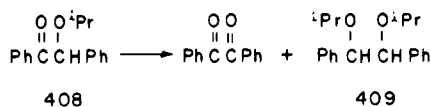
sions, benzil and **409** were formed in equal amounts in a reaction which could not be quenched by 1,3-cyclohexadiene, but could be sensitized by *m*-methoxyacetophenone (E_T = 72.4 kcal/mol). Phosphorescence spectra indicate that **408** has a lowest $n\pi^*$ triplet (E_T = 73.4 kcal/mol; τ = 30 msec).[289] Thus, a triplet state of **408**, which α-cleaves with a rate constant of $>10^{10}$ sec^{-1} is suggested to be involved in the reactions of **408**.[289] The reaction could also be sensitized by Michlers' ketone (E_T = 61.0 kcal/mol). This novel finding was attributed to α-cleavage of an exciplex formed from excited Michlers' ketone and **408**.[289] Sandner and Osborn studied the related 2,2-dimethoxy-2-phenylacetophenone, and found that a short-lived triplet state (E_T <69 kcal/mol) of this compound undergoes α-cleavage, with subsequent formation of radical products.[290]

Sheehan and coworkers investigated similar compounds as possible photochemically labile protecting agents.[291] They found that the deoxybenzoins substituted by leaving groups in the α position gave either α-cleavage or cyclization with aromatization.[291] For example, the acetoxyanisole derivative

	X	X'
a:	OAc	*p*-MeO
b:	NMe₃	H
c:	OAc	H
d:	OAc	*m*-MeO
e:	OAc	3,5-diMeO
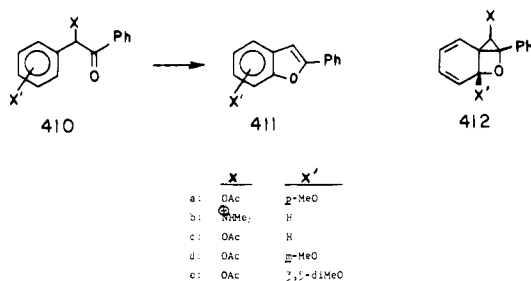
410a underwent exclusive α-cleavage via a triplet state as evidenced by piperylene quenching, while the benzene derivatives **410b** and **c** undergo cyclization and elimination in 70 and 20% yield, respectively.[291] In contrast to the *p*-methoxy derivative, the *m*-methoxy and 3,5-dimethoxy derivatives **410d** and **e** undergo cyclization to the benzofurans **411**; the latter occurs quantitatively with a quantum yield of 0.64 at 366 nm.[291] The possible intervention of oxetane **412** was suggested with methoxy enhancing the formation of **412** by increasing the nucleophilicity of the aromatic nucleus toward the electrophilic $n\pi^*$ excited state.[291]

In the 1-indanone series, Baum found that **413a** underwent α-cleavage and formation of the unsaturated aldehydes **414a** and **415a** in a ratio of 4:1 upon direct photolysis in benzene.[292] The reaction was sensitized by acetophenone and quenched by *cis*-piperylene, implying that a triplet excited state was photoreactive. Phosphorescence at 77°K indicated the $n\pi^*$ character of the lowest triplet (E_T = 74 kcal/mol; τ = 1 msec). The $^3n\pi^*$ state was unreactive in the absence of α-aryl substituents, because the analogs **413b** and **c**, both of which lack the α-phenyl substituent, were unreactive. Finally the biphenyl analog **413d** undergoes aldehyde formation very inefficiently, and this inefficiency was attributed to the fact

	R	R'
a:	Ph	H
b:	H	H
c:	Me	H
d:	Ph	Ph
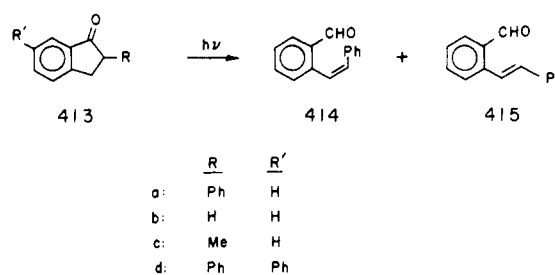
that this compound possesses a lowest $\pi\pi^*$ triplet state as indicated by phosphorescence spectra (E_T = 66 kcal/mol; τ = 5.5 sec).[292]

Recently, Heine, Lewis, and their coworkers have summarized the photochemical reactions of deoxybenzoins and have provided further studies of the photochemical α-cleavage reactions of deoxybenzoin, as well as the α-methyl, α,α-dimethyl, and α-phenyldeoxybenzoins.[293] The products formed were all accounted for by α-cleavage of the $n\pi^*$ triplet (phosphorescence studies), and subsequent efficient cage recombination which competes effectively with diffusion out of the cage and subsequent radical reactions. Notably, the rate of triplet α-cleavage of deoxybenzoin is about one-tenth that of pivalophenone, indicating that radical stabilities do not contribute significantly to the rate of α-cleavage. These authors propose an early "transition state" for α-cleavage in which the α-bond is only slightly stretched.

Benzoin ethers are industrially important photochemical initiators of polymerization. Their utility as initiators increases with α-alkylation, which increases the rate of α-cleavage from short-lived, unquenchable, presumed singlet $n\pi^*$ states.[165]

Hart and coworkers found further evidence for α-cleavage of α'-aryl-α,β-unsaturated ketones in the reactions of **416** and **418**.[295,296] The four compounds represented in these

	R₁	R₂	R₃
a:	H	H	H
b:	H	Me	H
c:	Me	H	H
d:	H	H	Ph
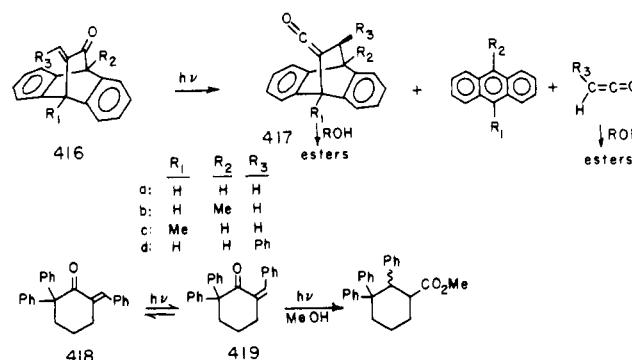
drawings give products of 1,3-benzhydryl shifts, undoubtedly the result of initial α-cleavage, followed by rotation and rebonding. Ketenes and anthracene are also formed. The ratio of cleavage to 1,3-shift was wavelength dependent; with **416d** at 350 nm, this ratio was 18:82, while at 300 nm, the ratio was 32:86. Hart et al. suggested that α-cleavage occurs from a $n\pi^*$ triplet state while the 1,3-shift occurs from an $\pi\pi^*$ triplet state. The ultraviolet spectrum of **416d** shows $n\pi^*$ maxima at 343, 363, and 383 nm, and a $\pi\pi^*$ maximum at 298 nm.[296] The monocycle **419** also gives the 1,3-shift product (benzhydryl migration).

Finally, Hart and Love found that the bicyclic compound, **420**, does not undergo a characteristic α-cleavage reaction, but instead undergoes a di-π-methane rearrangement.[297]

The α-aryl ketones undergo α-cleavage through either singlet or triplet states. The contrast with β,γ-unsaturated (alkenyl) ketones can be attributed to the $n\pi^*$ nature of the α-aryl ketone excited states, as compared with the $\pi\pi^*$ nature for the α-alkenyl ketones.

420

$* = CD_3$
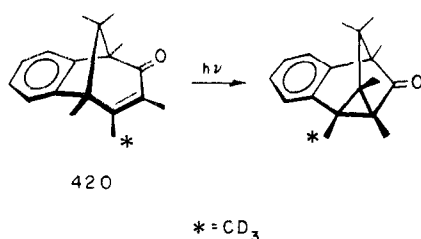
2. α-Aryl Aldehydes

Schaffner and coworkers have carried out extensive studies of α-aryl aldehyde photochemistry,[298-300] which complement their work on β,γ-unsaturated ketone photochemistry. The photochemistry is quite similar. Dimethylphenylacetaldehyde and its ring-substituted derivatives have been subjected to the most thorough investigations. Irradiation of the aldehyde 421a in dilute solution gives the decarbonylated products 422a and 423a in a ratio of about 6:1. An increase in concentration of the starting ketone results in increased yields of the dimeric product 423a.[298] Deuterated 421a gives

421   422   423
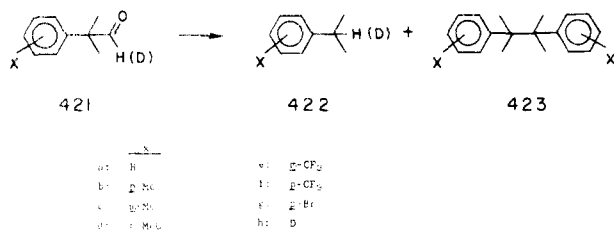
deuterated 422a and 423a in a ratio of 27:1. Deuteration thus has a pronounced effect on the ratio of products and favors formation of 422 over 423. All of the deuterium is retained in the cumene. However, irradiation of deuterated 421a in the presence of tri-n-butyltin hydride gives both the alcohol, formed by reduction of the excited ketone, and cumene with up to 30% of protium incorporation.

Irradiation of a mixture of deuterated 421a and 421h results in the formation of only monodeuterated products, indicating that the reaction to form 422 is exclusively intramolecular in the absence of added hydride. For the series of ring-substituted derivatives, small isotope effects on the rate of decarbonylation are found, ranging from 1.10 for 421a to 1.40 for 421d.[298]

Attempted quenching of the decarbonylation with piperylene or naphthalene failed, while irradiation in acetone gave none of the decarbonylated product. Quantum yields for the decarbonylation of the various derivatives of 421 were measured. For the parent compound 421a, wavelength dependence was observed ($\Phi^{254nm} = 0.64$; $\Phi^{313nm} = 0.76$). For the ring-substituted derivatives, quantum yields varied from 0.60 (m-CF$_3$) to 1.25 (p-Br), the latter value indicative of some incursion of a radical chain mechanism.[298] Irradiation of 421a in the cavity of an nmr spectrometer gave emission signals due to both the aldehyde proton in the starting material and the side-chain methine protons in cumene product.[299] The observation of emission requires that some fraction of the product formed in a polarized state arises from a triplet radical pair or from a diffusive encounter of formyl and cumyl radicals. The latter is excluded by the complete intramolecularity of the reaction, while the triplet pair is deemed unlikely since the bulk of the reaction cannot be sensitized. The authors conclude that only a minor fraction of the reaction involves a triplet pair, and that the major pathway is a concerted or near-concerted mechanism like that suggested earlier for the β,γ-unsaturated aldehydes.[299] The photolysis of other α-aryl aldehydes lends further credence to this mechanism.

TABLE XXVII. Quantum Yields for Decarbonylation of α-Aryl Aldehydes[244]

| Compd | (X) | Irradiation Wavelength | | | k_H/k_D |
		254 nm	313 nm	334 nm	
421a	(H)	0.64	0.76		
b	(p-Me)		0.80		
c	(m-Me)		1.00		
d	(p-MeO)		1.04		
e	(m-CF$_3$)		0.60		
f	(p-CF$_3$)		0.71		
g	(p-Br)		1.25		
h	(m-MeO)		0.76		
424a			0.02		
424b			0.39		
427a		0.29	0.11		
427b		0.073	0.065	0.11	
431a		0.70	0.43		1.09
431b		0.48	1.03		1.28
431c		0.17	0.90		1.02
431d					1.05

Aldehyde 424a gives the decarbonylation product 425a, while in the presence of tri-n-butyltin hydride, the cyclopropane cleaved products 426a and b are also formed. The cyclopentyl compound 424b gave the decarbonylation product 425b exclusively.[298] As shown in Table XXVII, the quantum yield for decarbonylation of the cyclopropyl compound 424a was far lower than that for the other compounds investigated.

424   a: $\frac{n}{2}$ 425   426
      b: 4

427   428

a: $\frac{R}{H}$

b: MeO

R
a: CHO
b: H
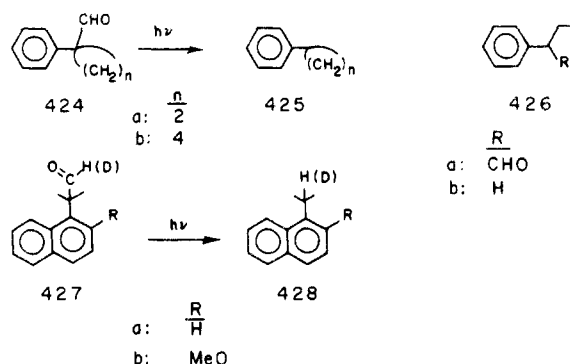
The α-naphthyl derivatives 427a and b also photodecarbonylate, but with lower efficiency than the α-phenyl compounds. Deuterium is retained quantitatively in 428a upon photolysis of deuterated 427a, while 5% protium incorporation is observed in 428b.[298] Irradiation of the deuterated 427a in the presence of tri-n-butyltin hydride gave less than 5% protium incorporation, while with 427b, more than 50% protium was incorporated.[298] Irradiation of 427a in the presence of 1,3-cyclohexadiene gave the dimers of the latter, indicative of triplet energy transfer from the aldehyde, but the efficiency of the decarbonylation was not decreased. Similarly, the aldehyde 427a quenches the photoreduction of benzophenone, but decarbonylation of 427a does not occur. These results imply that the decarbonylation is a singlet process and that the triplet is quite unreactive,[298] a rather startling contrast to benzyl ketones! However, the triplet state of benzene has an energy of about 85 kcal/mol, while that of naphthalene is about 61 kcal/mol, so that benzyl ketones are expected to have lowest $n\pi^*$ triplets (which readily α-cleave) while the naphthyl ketones will have lowest $\pi\pi^*$ triplets.

A correlation between the intensity of $n\pi^*$ absorption of these aldehydes and the quantum yields for decarbonylation was observed. Thus, in the series 421, electron-withdrawing substituents decrease the absorption intensity somewhat and also lower the quantum yields for decarbonylation. For most of these compounds, the extinction coefficients for the $n\pi^*$

TABLE XXVIII. Kinetic Isotope Effects and Quantum Yields of Decarbonylation of 431

Compd	k_H/k_D	$\Phi^{254}(-CO)$	$\Phi^{313}(-CO)$
431a	1.09	0.70	0.43
431b	1.28	0.48	1.03
431c	1.02	0.17	0.90
431d	1.05		

absorption are 100–300, but for the cyclopropyl compound **424a**, no enhanced $n\pi^*$ absorption is observed and the quantum yield of decarbonylation is lowest (Table XXVII). It was proposed that conformation **429** is required both for enhancement of absorption intensity and for efficient decarbonylation, and that the cyclopropyl compound prefers the conformation **430** which is unfavorable for both of these. Further-

more, the wavelength dependence observed (Table XXVI) can be explained by the assumption that only certain rotamers are efficiently decarbonylated and that selective excitation of these rotamers leads to more efficient decarbonylation.[298] Either a concerted reaction from a singlet state, or α-cleavage of the singlet with a 100% efficient cage recombination, is suggested to account for all these results. The "concerted" mechanism may actually involve the intimate radical pair postulated earlier to account for the alkenylaldehyde results.
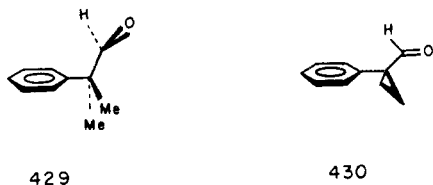
The photochemistry of the formylindan (**431a**) and its heterocyclic analogs **431b–d** provides further examples of the now well-established course of α-phenyl aldehyde photochemistry.[300] Thus, **431a** decarbonylates to form **432a** exclusively in degassed solution, and the deuterated compound gives complete deuterium retention. The reaction is neither sensitized nor quenched, implicating a singlet excited state, and, in the presence of tri-*n*-butyltin hydride, hydrogen is incorporated to a small extent. The hetero analogs **431b–d** behave similarly, except that in the case of the sulfur and oxygen analogs, 5–10% of the aromatized compounds **433b** and **c**, are formed, indicating that hydrogen abstraction by the formyl radical competes with hydrogen transfer from the formyl radical in these cases. The wavelength dependence of the reactions of **431b** and **c** parallels the earlier results and are given in Table XXVIII along with kinetic isotope effects observed. Longer wavelength irradiation results in more efficient decarbonylation. Only **431a** behaves anomalously in this respect. A study of the solvent effect on decarbonylation efficiency was also carried out for **431a**. Although the quantum yield varies from 1.0 (pentane or cyclohexane) to 0.36 (methanol), there is no correlation between solvent viscosity and the quantum yield of photodecarbonylation.[300] Ultraviolet
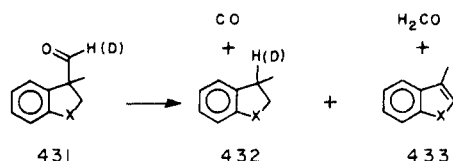
spectroscopic data for the α-aryl ketones and aldehydes discussed in the previous sections are given in Table XXIX.

3. Aryl Esters

The photo-Fries reaction of aryl esters has been the subject of intense scrutiny and has been reviewed recently.[235-237] Only a brief survey and some recent results will be given here.

Anderson and Reese reported the photo-Fries reaction of catechol monoacetate (**434a**) in 1960.[301] Both ortho (22%) and para (18%) products, along with catechol (46%), were formed in this reaction. Phenyl acetate (**434b**) behaves similarly.[301] Anderson and Reese suggested that diradicals **439** and **440** were intermediates in the 1,3- and 1,5-shifts, respectively.[301]
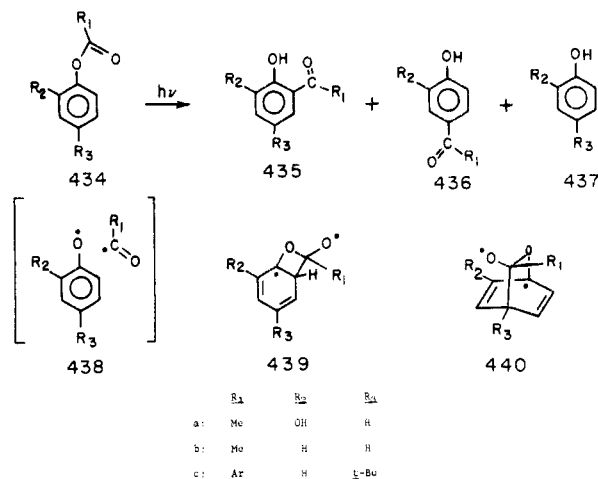
Kobsa carried out extensive studies of ten *p-tert*-butylphenyl aryl esters, **434c**, and suggested an alternative mechanism involving α-cleavage and formation of the radical pair **438**. The aryl esters formed 1,3-shift products **435c**, in good yields, and in some cases phenols or polymer were also formed.[302] Since the esters **434c** do not emit, Kobsa suggested that the α-cleavage occurred quantitatively, and cage recombination to **434** or to the dienone precursors to **435** and **436** occurred within the cage. This mechanism was also adopted by Finnegan and Mattice in their studies of 11 aryl esters.[303] According to this model, diffusion of the radical pair out of the solvent cage results in phenol formation. For a number of compounds of the general formula **434c**, quantum yields of about 0.65 were observed.[302]

A third mechanism was suggested by Saltiel, who postulated that electron transfer in excited **434** to an ion pair occurred.[304] Coppinger and Bell studied the quantum yields of rearrangement of 22 different aryl 3,5-di-*tert*-butyl-4-hydroxybenzoates impregnated in polyethylene films.[305] Because of the absence of fragmentation products and the substituent effects observed, a concerted mechanism was proposed.[305] A multiparameter "quasi-equilibrium" model was developed which gave a Hammett ρ of -2.45 for the effect of the aryl (phenoxy) substituents on the quantum yield of rearrangement. As an alternative to the concerted rearrangement mechanism, it was suggested that considerable charge transfer occurs in the excited state which leads to rearrangement.[305]

Sandner, Hedaya, and Trecker critically evaluated the proposed mechanisms and studied the dependence of quantum yields on various reaction parameters.[306] The reaction of *p*-tolylacetate provides an example of their data. The quantum yields for ester disappearance ($\Phi \sim 0.35$) and for 1,3-shift product formation ($\Phi \sim 0.17$) were insensitive to solvent hydrogen-donating ability, polarity, or viscosity, but the quantum

TABLE XXIX. Ultraviolet Spectra of α-Aryl Carbonyl Compounds

Compound	λ_{max}, nm (ϵ)	Solvent	Ref
Phenylacetone	258(255), 283(150)	95% EtOH	a
	260(235), 289(108)	C_6H_{12}	a
3-Phenyl-2-butanone	258(238), 283(226)	95% EtOH	a
	258(210), 289(177)	C_6H_{12}	a
1-Acetyl-1-phenylcyclopropane	260(245), 289(75)	EtOH	b
	260(205), sh284–285(50)	C_6H_{12}	b
1-Acetyl-1-phenylcyclobutane	261(294), 289(355)	EtOH	b
	261(238), 295(252)	C_6H_{12}	b
1-Acetyl-phenylcyclopentane	260(252), 291(292)	EtOH	b
	260(220), 296(217)	C_6H_{12}	b
1-Acetyl-1-phenylcyclohexane	260(250), 290(314)	EtOH	b
	260(208), 298(230)	C_6H_{12}	b
350k	260(430), 285(340)	MeOH	246
386h	253.2(245), 259(275), 265(251), 280(174)	C_6H_{14}	272
413a	324(92), 336(122), 353(101), 367(40)	MeC_6H_{11}	292
416a	246(5470), 280sh(3480), 284(4160), 309sh(149), 322(274), 355(460), 340(564), 367(503), 384(192)	C_6H_{12}	296
421a	259(243), 297(125)	EtOH	298
	259(260), 300(135)	C_8H_{18}	298
421b	265(396), 297(195)	EtOH	298
	265(359), 301(148)	C_8H_{18}	298
421c	265(326), 298(150)	EtOH	298
	265(290), 301(120)	C_8H_{18}	298
421d	275(1710), 300(301)	EtOH	298
	276(1280), 300(150)	C_8H_{18}	298
421e	263(689), 301(118)	EtOH	298
	263(560), 301(110)	C_8H_{18}	298
421f	264(396), 302(113)	EtOH	298
	265(336), 303(106)	C_8H_{18}	298
421g	268(328), 297(195)	EtOH	298
	269(445), 302(166)	C_8H_{18}	298
424a	258(209), 280sh(48)	EtOH	298
	258(196), 283(47), 292(35), 302(31), 312(22), 324(9)	C_8H_{18}	298
424b	261(470), 300(234)	EtOH	298
	262(355), 300(110)	C_8H_{18}	298
427a	270(14400), 281(17100), 292(11300), 313(990), 313(298)	EtOH	298
		C_5H_{12}	298
427b	284(6300), 295sh, 322sh, 336(2000)	EtOH	298

^{a} R. Gencarelli, H. Abajian, P. Irving, and S. MacKenzie, *J. Org. Chem.*, **35**, 2673 (1970). ^{b} S. MacKenzie, S. F. Marsocci, and H. C. Lampe, *ibid.*, **30**, 3328 (1965).

yield of p-cresol formation increased as solvent viscosity decreased. The authors suggested that the 1,3-shift is a photochemically allowed concerted $[1_s,3_s]$ sigmatropic shift involving an excited singlet state of the ester. Some α-cleavage, cage escape, and typical radical reactions must accompany this reaction. The Kobsa mechanism was considered to be experimentally untenable.[306]

Plank studied the photo-Fries rearrangements of phenyl benzoate and found that triplet sensitization was possible, and an increase in solvent polarity favored the formation of 1,3-shift product at the expense of the phenol.[307] A triplet excited state of E_T = 74–81 kcal/mol which α-cleaves to form phenol, or to a charge-transfer complex akin to Coppinger and Bells', and thence to the 1,3-shift product, is suggested.

Studies of the gas-phase photochemistry of phenyl acetate by Meyer and Hammond showed that little Fries product was formed, the principal products being the result of radical reactions.[308] In solution, the formation of a caged radical pair from a predissociative triplet state of the CO bond was suggested by Carroll and Hammond.[309]

Recent CIDNP studies of **441** also indicate that the caged radical pair mechanism operates in the photo-Fries reaction.[310] The photolysis of **441** in several solvents gave CIDNP effects compatible with formation of a singlet radical pair which recombines to form **441** and the ortho-Fries product in the cage. The radical also diffuses out of the cage, with formation of phenol.[310] The observed enhancement factors made competition of a concerted mechanism unlikely.[310]

Thus, the balance of the evidence appears to favor reaction from a singlet excited state and formation of a caged radial pair which recombines at a rate much faster than escape from the cage.

Kalmus and Hercules recently reported flash photolysis studies of the photochemistry of phenyl acetate and critically reviewed the mechanistic evidence amassed for the photo-Fries reaction.[311] The quantum yields for the formation of phenol increased from 0.09 in ethanol to 0.23 in hexane, compatible with a cage escape mechanism for phenol formation. The quantum yield of o-hydroxyacetophenone was relatively solvent insensitive (0.14–0.18), while that of p-hydroxyacetophenone dropped from 0.10 in ethanol to 0.05 in hexane. The absence of fluorescence and failure of quenching and sensitization experiments led to the conclusion that the photo-Fries reaction involves very efficient α-cleavage from an excited singlet state, very rapid in-cage recombination at oxygen or the ortho carbon, a slower in-cage combination at the para position, and diffusion out of the cage followed by phenol formation.[311]

TABLE XXX. Ultraviolet Spectra of Aryl Esters

Compound	λ_{max}, nm (ϵ)	Solvent	Ref
Phenyl acetate	212	C_6H_{14}	316
	259(230), 266	EtOH or $C_2Cl_3F_3$	311
Phenyl benzoate	240(12600), sh280(1000)		

TABLE XXXI. Ultraviolet Spectra of
β,γ-Unsaturated Aminoboranes

Compound	λ_{max}, nm (ϵ)	Ref
449	262(374), 269(376), 276(265)	317
450	262(340), 269(378), 276(293)	317

Evidence for mechanisms other than the cleavage–recombination keeps cropping up in some systems. Humphrey and Roller reported the flash photolysis of several aryl esters.[312] While the phenoxy radical was a detectable intermediate in the photo-Fries rearrangement of p-tert-butylphenyl benzoate, several cyclic analogs gave transients identified as Anderson–Reese-type bridged intermediates.[311]

Certain classes of aryl esters undergo anomalous reactions. Finnegan and Knutson found that highly hindered aryl esters undergo decarboxylation accompanied by the normal processes.[313] Both 442 and 443 give 4–14% of the decarboxylation products upon irradiation. In order to determine whether the decarboxylation was concerted, the irradiation of the optically active compound 444 was carried out. Irradiation in several solvents gave the phenol 447 as the major product, along with 0–15% of the decarboxylation product 445, which was optically active and had the retained configuration. A concerted decarboxylation was proposed. By contrast, the ether 446, formed in low yield, was racemic, consistent with formation from radical-pair recombination.[314]

441 442 443

444 445 446 447
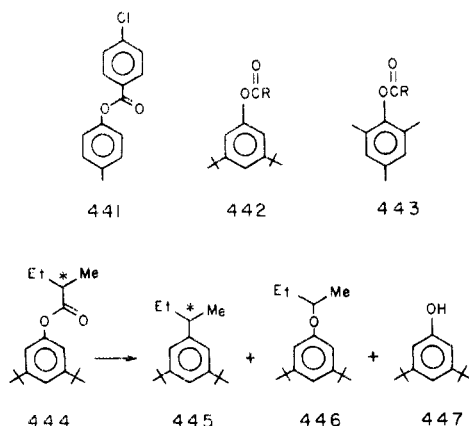
Aryl carbonates 448 also undergo the photo-Fries rearrangement.[315] The quantum yields for reactions of 448a,b, and c, are 0.21, 0.02, and 0.20, respectively. This is the order expected if methoxyl stabilization of phenoxy radicals were important.[315]

448

X
a: o-MeO
b: M-MeO
c: p-MeO
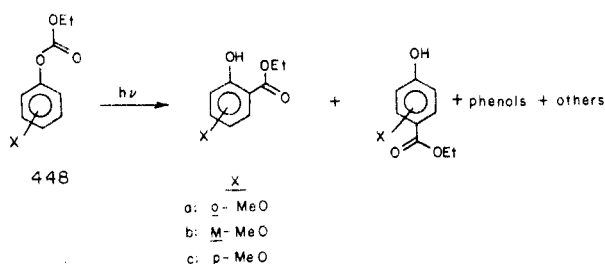
Finally, a number of rearrangements of anilides and related species have been discovered, and, where available, mecha-

nistic evidence is similar to that obtained for aryl esters.[235-237]

The ultraviolet spectra of two aryl esters are given in Table XXX. These compounds have weak $n\pi^*$ absorptions at moderately short wavelength and much stronger $\pi\pi^*$ bands at 8–10 nm longer wavelength than the corresponding aromatics.[316]

P. β,γ-Unsaturated Aminoboranes

An analogy to the photochemistry of β,γ-unsaturated ketones was found in the 1,3-shift of 449 to 450 observed by Hancock and Kramer.[317] These authors found that a photostationary state of 40:60 of 449:450 was formed upon irradiation of either 449 or 450. The quantum yields for the forward

449 450
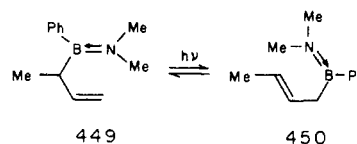
and reverse reactions were both 0.15, and the photostationary state ratio was determined by these equal quantum yields and the difference in extinction coefficients at 254 nm (Table XXXI). It was concluded that these reactions involved singlet states, since attempted sensitization led to a different product whose structure was not determined.[317] Interestingly, 449 and 450 are also interconverted by thermal 1,3-sigmatropic shifts.[318] The corresponding α-phenylaminoboranes were found to undergo singlet state cis–trans isomerization,[319] or, in CCl_4, to undergo α-cleavage reactions.[320] The analogy to carbonyl reactions and the apparent deviation from the corresponding alkene reactions led Hancock to suggest that photochemical 1,3-shifts might occur not only from $n\pi^*$ singlet states, but from $\pi\pi^*$ or $\sigma\pi^*$ states when $n\pi^*$ states were unavailable.[317]

Ultraviolet spectra of several aminoboranes are given in Table XXXI. The weak bands arise from $\sigma_{CB}\pi^*_{BN}$ transitions, so that the resemblance to carbonyls is perhaps quite close (see theory section).

Q. Brief Comparison with Di-π-methane Photochemistry

The photochemistry of the all-carbon analogs of the β,γ-unsaturated carbonyls has been extensively studied. An excellent recent review of di-π-methane photochemistry can be consulted for details and leading references.[88] The salient features of di-π-methane photochemistry, most of which have been revealed by Zimmerman and coworkers, will be described here where relevant to β,γ-unsaturated carbonyl photochemistry. The reader is referred to the review by Hixson, Mariano, and Zimmerman for further details.[88]

Di-π-methane rearrangements most generally take place via excited singlet states in acyclic or semicyclic systems, whereas cyclic systems rearrange via the excited triplet, as shown in the two classic examples in Figure 9.

In the case of cyclic compounds such as barrelene, the failures of excited singlets to undergo di-π-methane reactions are attributed to the facile occurrence of alternative reaction paths such as [2 + 2] photocycloadditions. The acyclic trip-
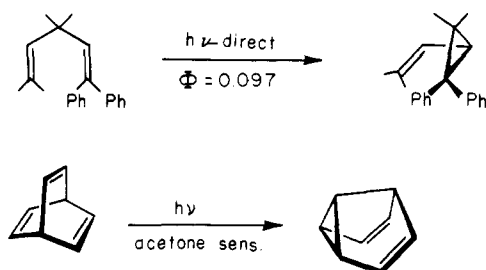
Figure 9. The di-π-methane rearrangement.

lets do not react because of the "free-rotor" effect; that is, the excited triplets undergo rotation about an unconstrained double bond. This process efficiently deactivates the excited state before reaction can occur. It has also been suggested that the isomerization may occur by initial π–π bonding, followed by rotations in the diradical, and then collapse of the diradical back to starting material.[88] As with di-π-methanes, some acyclic β,γ-unsaturated ketones do undergo the oxa-di-π-methane rearrangement, but the quantum efficiencies of such processes have not been studied. The effect has also been invoked to account for the lack of triplet reactivity in acyclic β,γ-unsaturated ketones. Thus, the di-π-methane rearrangement can occur from either $^1\pi\pi^*$ or $^3\pi\pi^*$ excited states, but alternative pathways may compete in specific structural types. The oxa-di-π-methane reaction undoubtedly occurs via a triplet state best described as $\pi\pi^*$ (see later), so that the analogy between the two reactions is apt.

Other features of the di-π-methane rearrangement are shared by the oxa-di-π-methane rearrangement; both are highly regiospecific, and in the case of 1,4-dienes the singlet reactions give migration of the less conjugated moiety. For the first example shown in Figure 9, Zimmerman suggested that the initial diradical intermediate (or its equivalent point on a concerted reaction hypersurface) opens to form the more stabilized diradical. That is, the direction of cleavage is governed by the principle of "maximum odd-electron stabilization". A similar explanation is required to account for the formation of only cyclopropyl ketones, and not vinyl oxiranes, from the analogous diradical shown in Figure 10. In this case, the exclusive cleavage to A is not highly favored by odd-electron stabilization, but the gain in carbonyl group bond strength over that of an alkene double bond further facilitates cleavage to form A. Although vinyl oxiranes are sufficiently thermally stable to be isolated,[321] they have never been observed in β,γ-unsaturated carbonyl photochemistry. The triplet rearrangement regiospecificity of 1,4-dienes has been rationalized on the basis of relative triplet energies of involved moieties.[322]

It has been found that substitution of the central carbon of a di-π-methane system can have a pronounced effect on reactivity.[322] Systems lacking this substitution undergo the di-π-methane rearrangement reluctantly, presumably owing to the lack of stability afforded the "unzipped" species formed after initial π–π bonding. Furthermore, if the central carbon is substituted with two phenyls, the "free rotor" deactivation of the triplet state is overcome, presumably because of the activation caused by stabilization of the "unzipped" diradical by the phenyls. Recently, Zimmerman and coworkers have been able to measure the absolute rate constants for a number of di-π-methane reactions.[323] These measurements indicate that the facility of the initial π–π bridging step determines the rate of singlet state di-π-methane rearrangements.

R. Stereochemistry of Oxa-di-π-methane and Di-π-methane Rearrangements

The stereochemistry of the singlet di-π-methane rear-
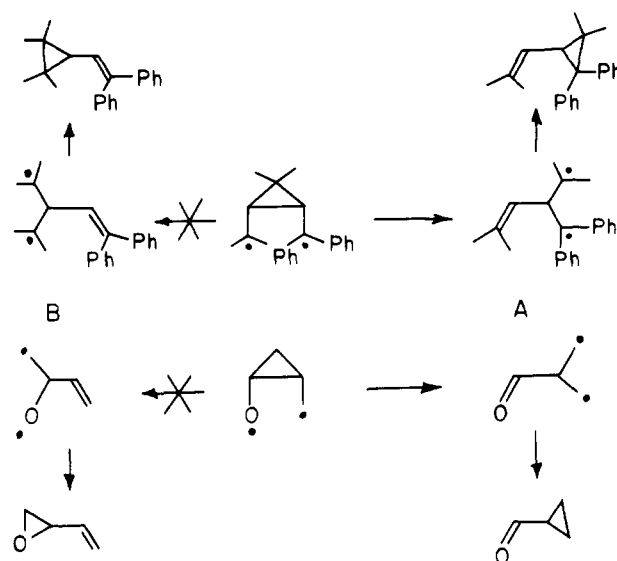
Figure 10. Regiospecificity in di-π-methane and oxa-di-π-methane rearrangements.

anti - disrotatory   syn-disrotatory   possible intermediate A
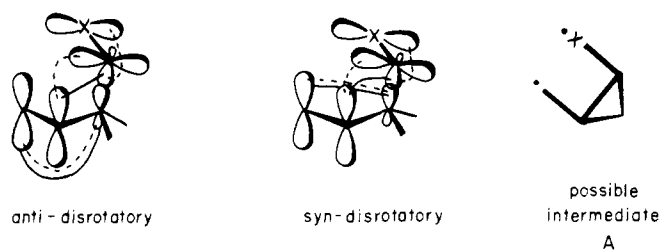
Figure 11. Allowed stereochemical modes for the di-π- and oxa-di-π-methane rearrangements. *Anti-disrotatory:* (- - -) $[_\pi2_a + _\sigma2_a + _\pi2_a]$, (—) $[_\pi2_a + _\sigma2_a]$. *Syn-disrotatory:* (- - -) $[_\pi2_s + _\sigma2_s + _\pi2_a]$, (—) $[_\pi2_s + _\sigma2_s]$. A is a possible intermediate in this transformation.

rangement has been found to be preferentially the "anti-disrotatory" shown in Figure 11, although the "syn-disrotatory" reaction occurs if the former is sterically prevented. Figure 11 shows the stereochemistry of bond making for the two modes as well as the analyses of these reactions in terms of orbital symmetry. The anti-disrotatory mode may be considered either a photochemically allowed $[_\pi2_a + _\sigma2_a + _\pi2_a]$ reaction or a $[_\pi2_a + _\sigma2_a]$ reaction. Zimmerman favors the first mechanism (involving the CX multiple bond), since systems lacking this double bond undergo rearrangement much less efficiently than the di-π-methane systems. Recently, definitive evidence for inversion of configuration at C-3 of a acyclic chiral 1,4-diene has been obtained.[324] This result is particularly important, since this acyclic system was not sterically constrained to undergo the reaction with inversion at C-3. Furthermore, the stereospecific nature of the reaction indicates that no long-lived diradical such as A can be an intermediate in the rearrangement. The oxa-di-π-methane rearrangement stereochemistry has been investigated in several cases. Table XXXII summarizes these observations. For a completely unconstrained system, there are 16 possible stereochemical modes of reaction. Those involving migration of the acyl moiety from the "top" of C_α to "bottom" of C_β, a distinctly unlikely process, have been excluded from consideration. The majority of the 1,2-shifts involved constrained systems which must undergo the "anti-dis" stereochemistry. In less constrained systems, both the syn-dis and anti-dis stereochemistries have been observed. The secondary stereochemistries observed are potentially of import. Thus both β-**95a**, and β-**95b**, prefer to rearrange through conformations in which the carbonyl and γ-carbon of the alkene are near each other (syn) rather than those in which these groups are further re-

TABLE XXXII. Stereochemistry of the Oxa-di-π-methane Rearrangement

Compound	Sterically permitted stereochemistries[a]	C$_\alpha$ stereochemistry[b]	Secondary stereochemistry[c]	Exptl results	Ref
265[d]	syn-dis	r			183
	anti-dis	i		Obsd	
128a[d]	anti-dis	i	β		49
	anti-dis	i	α	Obsd	
	anti-con	r	β		
	anti-con	r	α	Obsd[e]	
256b	anti-dis	i	β	Obsd	179
	anti-dis	i	α	Obsd	
	anti-con	r	β	Obsd[e]	
	anti-con	r	α	Obsd[e]	
β-95a and α-95a[d]	anti-dis	i	anti		55
	syn-dis	r	syn	Obsd[f]	
	anti-con	i	syn		
	syn-con	r	anti	(Obsd)[f]	
159c	anti-dis	i	syn		112
	anti-dis	i	anti	Obsd	
174a, 174e, and 174f	syn-dis	r		Obsd[g]	115
	anti-dis	i		Obsd[h]	
Polycyclic systems such as bicyclo[2.2.2]octenone	anti-dis	i	anti	Obsd	See text

[a] The "con" stereochemistries are orbital symmetry forbidden modes. "Anti-con" designates the stereochemistry in which the lobe of the p orbital near the acyl group rotates away from the acyl group. [b] r = retention; i = inversion. [c] β = acyl migrates along β-face of the steroid; α = acyl migrates along α face; syn = reaction conformation has C$_\gamma$ near the carbonyl oxygen; anti = reacting conformation has C$_\gamma$ away from the carbonyl oxygen. [d] The modes not sterically permitted are those giving transfused cyclopropanes. [e] This stereochemistry may result from isomerization of the cyclopropyl ketone product.[49,179] [f] Since there are no labels on C$_\gamma$, either syn-dis, or syn-con mechanisms are compatible with the observations. [g] Isomerization of the cyclopropyl ketone product has been ruled out for this stereochemistry.[115] [h] The anti-dis stereochemistry is favored by 5:1, 7:1, and 3:1 in 174a, 174e, and 174f, respectively.[114]

moved. **159c** prefers the opposite (anti) conformation. One acyclic case apparently prefers neither.[454]

It is interesting that the stereochemical comparisons made here are of the *singlet* di-π-methane and *triplet* oxa-di-π-methane rearrangements. The stereochemistry of the triplet di-π-methane reaction is less well established, but one case where the cis,trans isomerization of the migrating alkene accompanies rearrangement is known.[88] This type of stereochemistry is, of course, invisible in the oxa-di-π-methane rearrangement.

One interesting feature of most studies of di-π-methane and oxa-di-π-methane rearrangements is that no long-lived diradical such as A (Figure 11) can be involved, since stereochemistry of the radical centers should be lost by rotation about a single bond (see, however, ref 454). Several examples of such stereochemical scrambling have been reported for oxa-di-π-methane rearrangements, and in Schaffner's examples (**174**) product isomerism has been ruled out, but no long-lived diradical corresponding to the "second" diradical (A or B in Figure 10) in the di-π-methane rearrangement can be formed, since a different product ratio is obtained from its formation by thermal means,[114] or by photolysis of a different precursor.[28,34]

III. Spectroscopy and Theories of Spectra of β,γ-Unsaturated Carbonyls

A. Geometrical Definitions

In order to facilitate the discussion of the dependence of orbital interactions and photoreactions on the geometry of the β,γ-unsaturated carbonyl moiety, the definitions shown in Figure 12 will be used. These conventions are those adopted by Hoffmann and coworkers in their theoretical investigations of α-amino ketones[325] and are adopted here to facilitate comparison with these related systems. The angle φ is defined as the dihedral angle between the C–O bond and the α,β bond, while the angle θ is the dihedral angle between the bond α to

φ   θ

(0,0)   (0,90)   (0,180)

(90,0)   (90,90)   (90,180)

(180,0)   (180,90)   (180,180)

(270,0)   (270,90)   (270,180)
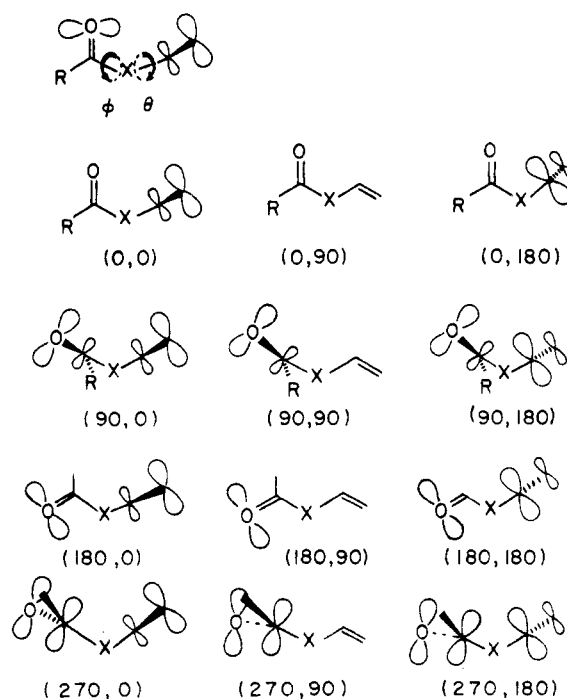
Figure 12. Definitions of β,γ-unsaturated carbonyl geometries.

the carbonyl and the π orbital of the CC double bond. The definitions of zero for φ and θ are chosen to coincide with those in the work of Hoffmann. In the latter work, the interaction of the lone pair on nitrogen with the carbonyl n orbital was of interest. For the β,γ-unsaturated carbonyls, the angles are chosen so that the π bond is eclipsed with the α bond for θ = 0°. Figure 12 also gives some representative geometries.
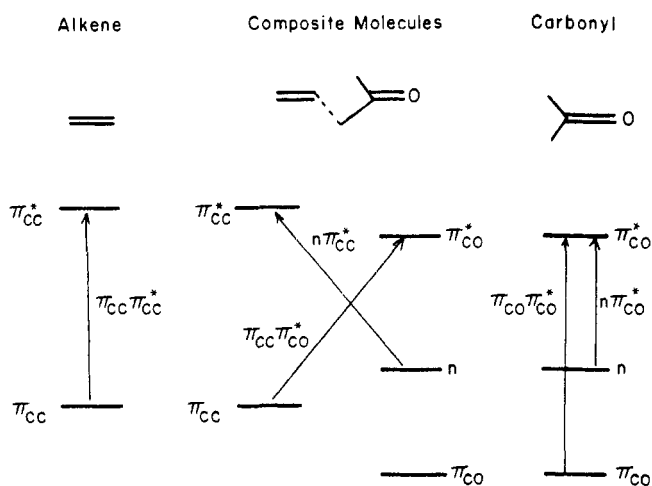
Figure 13. Murrell's excitation delocalization model of β,γ-unsaturated ketone electronic transitions.

Figure 14. The molecular orbital model of β,γ-unsaturated ketone electronic transitions (Labhart and Wagniere).

B. Theories of β,γ-Unsaturated Carbonyl Electronic Spectra

Three theoretical treatments of the spectroscopy of β,γ-unsaturated ketones are of particular value in both defining the spectroscopic nomenclature to be used in this section and in understanding the origin of the enhanced absorptions and "charge-transfer" transitions observed for these species in some geometries. The first theoretical treatment of these phenomena by molecular orbital methods by Labhart and Wagniere[326] followed Cookson and Wariyar's empirical observations about the electronic and geometrical requirements for $n\pi^*$ intensity enhancements.[327]

1. Murrell's Excitation Delocalization Model[328]

The Murrell excitation delocalization model facilitates comparison of electronic transitions in the β,γ-unsaturated carbonyls with those in isolated alkenes and carbonyl compounds. Figure 13 shows schematically the Murrell model[328] which is based on the theoretical methods developed by Longuet-Higgins and Murrell.[329] The transitions of interest are the $\pi\pi^*$ transition for both the alkene and carbonyl moieties, and the $n\pi^*$ transition for the carbonyl moiety. The composite molecule can have these transitions (which have been omitted from Figure 13, for clarity) and the $n\pi^*_{CC}$ and $\pi_{CC}\pi^*_{CO}$ charge transfer transitions shown in the composite molecule diagram.

Murrell's explanation of intensified $n\pi^*$ transitions can be summarized as follows: A direct interaction of the $n\pi^*_{CO}$ and $\pi_{CC}\pi^*_{CC}$ transitions can lead to little intensification of the $n\pi^*_{CO}$ transition owing both to the fact that the $n\pi^*_{CO}$ transition is forbidden and to the fact that there is a large difference in these transition energies ($\Delta E_{\pi_{CC}\pi^*_{CC}} \approx 6$ eV, $\Delta E_{n\pi^*_{CO}} \approx 4$ eV). However, intensification will result if the $n\pi^*_{CO}$ transition interacts with and borrows intensity from a second, relatively intense, transition involving either the n or π^*_{CO} orbitals. Thus, the $n\pi^*_{CO}$ transition can be intensified by interaction with either the $\pi_{CC}\pi^*_{CO}$ or the $n\pi^*_{CC}$ charge-transfer transitions. The extent of interaction of the $\pi_{CC}\pi^*_{CO}$ transition with the $n\pi^*_{CO}$ transition will depend on the extent of overlap of the π_{CC} and n orbitals, while interaction of the $n\pi^*_{CC}$ and the $n\pi^*_{CO}$ transitions will depend on the overlap of the π^*_{CC} and π^*_{CO} orbitals. A second factor, namely the intensity of the charge-transfer transition from which intensity is to be borrowed, must be considered. The intensities of such transitions depend on the extent of overlap of the donor and acceptor orbitals. For the model 2-norbornenone used by Murrell, overlap of the π_{CC} orbital with the π^*_{CO} orbital is much larger than
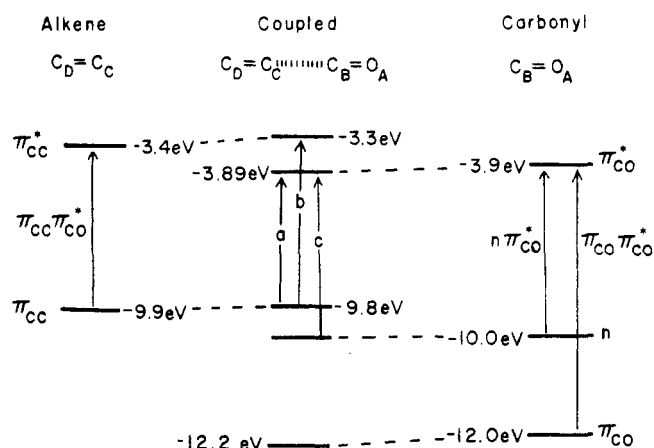
that of the n orbital with the π^*_{CC} orbital, so that for β,γ-unsaturated ketones with geometries like that of 2-norbornenone, a fairly strong $\pi_{CC}\pi^*_{CO}$ charge-transfer band should be observed, and the $n\pi^*_{CO}$ band will be intensified if there is also overlap of the n orbital with the π_{CC} orbital.[328] In terms of the geometry definitions (Figure 12), 2-norbornenone has approximately a (110°, 200°) geometry. The β,γ-unsaturated ketones which have $n\pi^*$ intensifications usually also have observable charge transfer (CT) bands at 200–220 nm. In support of Murrell's explanation, 7-norbornenone, which does have a 220-nm CT band, has a normal intensity $n\pi^*$ band. In this case, the n and π_{CC} orbitals cannot overlap since they are of opposite symmetry.[328]

In this excitation delocalization model, intensification of the $n\pi^*_{CO}$ transition depends on $\pi^*_{CC}-\pi^*_{CO}$ overlap, which varies as $|\sin\phi|$ and $|\cos\theta|$, and also on $n-\pi_{CC}$ overlap, which varies as $|\cos\theta|$, assuming the $n-\pi_{CC}$ interaction is a purely "through-bond" interaction (vide infra). Thus, maximum intensification should occur in a β,γ-unsaturated ketone with $\phi = 90$ or $270°$, and $\theta = 0$ or $180°$. The model compound, 2-norbornenone, studied by Murrell, has nearly an ideal geometry (110°, 200°) for both charge transfer and enhanced $n\pi^*_{CO}$ absorptions.

2. The Labhart–Wagniere Molecular Orbital Model[326]

The earlier Labhart and Wagniere model is based on a molecular orbital treatment, but arrives at a conclusion similar to that of Murrell. Labhart and Wagniere calculated the transition energies and intensities which would result from mixing of the π orbitals of an isolated alkene with the π orbitals and n orbital of a carbonyl compound. Thus, a delocalized ground-state model was used, whereas Murrell considered only delocalization of excitation. Labhart and Wagniere started with the orbital energies shown in Figure 14 and calculated the various transition energies and intensities as a function of overlap of the two fragments. They were concerned with explaining both the appearance of a new band around 220 nm and the intensification of the $n\pi^*$ absorptions in some β,γ-unsaturated ketones. The orbital energies were assigned from ionization potentials and transition energies (a one-electron model was used), and the molecular orbitals formed from interaction of these orbitals were found by assuming that the interaction was proportional to overlap. As the π systems of the alkene and the carbonyl overlap more strongly, a "charge-transfer" transition between alkene π and carbonyl π^* orbitals intensifies and shifts to longer wavelength. Thus, the β,γ system is treated as a stretched α,β-unsaturated ketone but an explanation of the "charge-transfer band" similar to that of Murrell is obtained. Labhart and Wagniere suggested that the intensif-

ication of the $n\pi^*$ transition arises as a result of the overlap of the n orbital on oxygen with the p orbitals of the alkene double bond. Since the π_{CC} and n orbitals are of similar energy before interaction, they mix, removing the symmetry forbiddenness of the $n\pi^*$ transition. Figure 14 shows the results diagrammatically. Since the allowedness of a transition depends on overlap, α,β-unsaturated ketones, which have strong p_b-p_c overlap, but not p_n-p_c overlap, have the "CT" transition (a), but do not have the intensified $n\pi^*$ transition. Using the perturbation language which is currently applied to phenomena of this type,[330] the π^*_{CO} orbital mixes in some of the π^*_{CC} orbital in a bonding fashion. In the limit of complete bond formation, the charge-transfer transition (a) becomes the $\pi\pi^*$ ($\Psi_2 \rightarrow \Psi_3$) transition of an α,β-unsaturated ketone. The energy levels shown in Figure 14 were obtained for a bicyclo[2.2.2]octenone model, where the overlap of p_c and p_b is about one-fourth that in an α,β-unsaturated ketone. For this model, the calculated transitions are: (a) a $\pi_{CC}\pi^*_{CO}$ charge transfer transition at 210 nm with $f = 1.50$, (b) a $\pi_{CC}\pi^*_{CC}$ transition at 192 nm with $f = 2.29$, and, (c) an $n\pi^*_{CO}$ transition at 275 nm with $f = 0$.

The $n\pi^*_{CO}$ transition becomes a transition from an n orbital mixed with some of the π_{CC} orbital to the π^*_{CO} orbital mixed with some of the π^*_{CC} orbital. The orbitals involved are not orthogonal by symmetry, and, therefore, some allowedness (calculated as about 0.01 that of an allowed transition, for bicyclo[2.2.2]octenone) is conferred on this transition.[326]

Predictions based on either the Labhart–Wagnieré or Murrell models are nearly the same. For the geometries defined in Figure 12, the charge transfer transition should vary as $|\sin \phi|$ and $|\cos \theta|$. If the n–π_{CC} interaction were only of the through-space type, it would be a maximum for the $\phi = 0°$ and $\theta = 0$ or $180°$ geometries and would fall off rapidly as ϕ was varied. However, for a through-bond interaction[325,330] involving the σ-bond α to the carbonyl, a $|\cos \theta|$ dependence only would be observed.

3. Moscowitz's Configuration Interaction Model

Moscowitz and coworkers proposed a model for β,γ-unsaturated ketone spectra[331] which is similar to the Murrell model, but arrives at significantly different conclusions. To account for the spectrum of 2-norbornenone, the ionization potentials and excitation energies for norbornene and 2-norbornanone were used, and configuration interaction between the various one-electron excitations was calculated. A delocalized model for the n orbital (with significant density on the adjacent carbon) was used, and although the dihedral angles used in this calculation are not stated explicitly, they appear to be $\phi = 240°$ and $\theta = 330°$.

Using estimated interchromophoric β's and electron repulsion integrals, both the enhanced $n\pi^*$ absorption intensity and the rotational strength could be accounted for by the mixing of local $n\pi^*_{CO}$ and $\pi_{CC}\pi^*_{CC}$ transitions. The contribution of charge-transfer states to the $n\pi^*$ state was negligible. The enhancement arose mainly from electrostatic interaction of the transition dipoles, since setting the interchromophoric β's to 0 caused a negligible decrease in the mixing of the $n\pi^*_{CO}$ and $\pi\pi^*_{CC}$ transitions.[331]

Moscowitz et al. pointed out that the success of the Labhart–Wagniere model probably stems from the fact that the overlap of the n and π_{CC} orbitals, considered by Labhart and Wagniere to cause the $n\pi^*$ enhancement, parallels the electrostatic repulsion integrals between these orbitals, considered by Moscowitz to be the cause for enhancement.

The disagreement of Murrell's treatment[328] and that of Moscowitz et al. is of some interest, since both utilized the Longuet–Higgins–Murrell formalism[329] to investigate the origin of the $n\pi^*$ enhancement. Murrell states that the interaction of

$n\pi^*$ transition with the $\pi\pi^*$ transition can lead to an enhancement of no more than 2, while Moscowitz et al. attribute essentially all of the enhancement to this interaction.[331] This discrepancy probably arises from the fact that Moscowitz used a delocalized model for the orbital, while Murrell used an essentially localized model for the n orbital. That is, Moscowitz allowed "through-bond" interactions, now known to be very important in interactions of nonconjugated chromophores. On a practical level, all three models discussed here predict essentially the same dependence of enhancement on geometry.

Several further comments on the disparities between and the congruencies among these various models are in order. The molecular orbital model of Labhart and Wagniere allows maximum interaction between the one-electron orbitals (both filled and vacant) and treats electronic transition energies as energy differences between one-electron orbitals. The "charge-transfer" nature of the $n\pi^*$ transition comes in because the "n" orbital is a delocalized orbital including both n and π_{CC} character, while the π^* orbital is mainly π^*_{CO} in nature. However, since the π^*_{CO} orbital admixes some of the π^*_{CC}, it is perhaps a matter of taste whether one considers the enhancement to arise from "charge transfer" or from admixture with the $\pi_{CC}\pi^*_{CC}$ transition.

The excitation delocalization, or configuration interaction, model, considers the ground state to consist of localized orbitals, and takes into account only the interaction between the various possible singly excited states. In such a treatment, electronic configurations rather than individual orbitals with charge-transfer configurations are discussed, but the ground state would be altered (stabilized by mixing). Semiempirical treatments of β,γ-unsaturated carbonyl spectra to be discussed later include both ground-state delocalization and configuration interaction between singly excited states, and from such a treatment, more detailed insight is, in principle, obtainable.

4. Applications of the Labhart–Wagniere Model to ORD and CD Spectra

Moscowitz et al. have applied both the Labhart–Wagniere and the configuration interaction models of β,γ-unsaturated ketones to the explanation of exalted rotational strengths in these systems.

In the Labhart–Wagniere model, the sign and magnitude of the rotational strength are determined by the sign and extent of overlap of the n and π_{CC} orbitals. The $n\pi^*$ transition of an achiral ketone is electric dipole forbidden, but magnetic dipole allowed. Perturbations of the $n\pi^*$ transitions which produce a nonzero electric dipole transition moment along the CO bond induce rotational strength, the magnitude of which will depend upon the extent of n–π_{CC} mixing. Thus, three conditions are necessary for large rotational strengths: (i) the π_{CC} and π_{CO} systems must overlap to give an "extended chromophore"; (ii) the n and π_{CC} orbitals must overlap; and (iii) the electric dipole transition moment (μ_e) must be as nearly parallel as possible to the magnetic dipole transition moment (μ_m). Since μ_e will be approximately colinear with the CC bond, an additional geometrical constraint is imposed for large rotational strengths. The theoretical treatment predicts a sign of the rotational strength in agreement with those observed for a number of compounds studied and leads to a modified octant rule which indicates that a β,γ-double bond will dominate the sign of the Cotton effect in the usual way. That is, a double bond in the back right octant will cause a negative Cotton effect (subject to i and ii alone) which will override the influence of other substituents.

In further studies, the CD spectra were found also to be diagnostic of the chirality of the inherently dissymmetric β,γ-

unsaturated carbonyl chromophore.[333] A positive sign of molecular ellipticity indicates a double bond in the back left octant.

Moscowitz and coworkers have applied the configuration interaction approach to the calculation of ORD and CD spectra.[332,334] The enhanced rotational strengths, like the enhanced absorptions, of some β,γ-unsaturated ketones are attributed to mixing of local $n\pi^*$ and $\pi\pi^*$ transitions. The CI approach is considered by Moscowitz to be more satisfactory than the molecular orbital treatment, since the sign of the rotational strength is not a sensitive function of orbital energies in the CI treatment.

Since the rotational strength is dependent on the $\pi_{CC}-\pi_{CO}$ overlap and the $n\pi_{CC}$ overlap (or the electron-repulsion integrals between these orbital pairs), the $|\sin\phi|$, $|\cos\theta|$ dependence noted earlier for $n\pi^*$ enhancement will hold for rotational strengths also. The additional requirement that the electric transition dipole, which is pointed along the CC bond, be parallel to the magnetic transition dipole, which points along the CO bond, is also satisfied quite well by the $|\sin\phi|$, $|\cos\theta|$ dependence.

5. Semiempirical Calculations on α-Aminocarbonyls and β,γ-Unsaturated Carbonyls

Although several theories to explain the β,γ-unsaturated ketone spectra have been discussed in the previous sections, the spectral interpretations which have been proposed are mainly qualitative in character. A series of calculations of orbital interactions in α-amino ketones and β,γ-unsaturated ketones have been carried out which attempt to deal with orbital interactions as a function of geometry on a more quantitative basis. Both of these are treatments built upon the concept of through-bond and through-space interactions elegantly espoused by Hoffmann and coworkers.[330]

Hoffmann et al. investigated the orbital interactions in α-aminoacetaldehyde and α-aminoacetone by ab initio (STO-3G) and extended Hückel (EHT) methods, respectively.[325] The geometrical definitions used by these authors were identical with those used here in Figure 12, except that the amino lone pair (sp^3 hybridized) is eclipsed with the C_1-C_2 bond of aminoacetaldehyde in the $\theta = 0°$ geometry, whereas the π orbital of the alkene moiety is eclipsed with the same bond in the $\theta = 0°$ geometry of β,γ-unsaturated carbonyl compounds.

The interactions of the n orbitals on oxygen and nitrogen were followed by tracing orbital energies as a function of geometry. For all geometries calculated with usual bond angles, the "n_S" orbital is of higher energy than the "n_A" orbital. These orbitals are represented qualitatively in Figure 15. The "n_S" orbital is the antibonding union of the n_O and n_N orbitals to a σ_{CC} level, whereas the n_A orbital is essentially the noninteracting "antisymmetric" combination of n orbitals. Although not explicitly stated by Hoffmann, the n_A orbital is probably more heavily localized on nitrogen than on oxygen. The only σ bonds which could interact with the n_A level (if it were rigorously antisymmetric with respect to a bisecting plane) would be σ^*_{CC} levels; these are much different in energy from the n_A level, so mutual interaction will be small. When θ is fixed at $0°$ and ϕ is varied from 0 to $90°$, there is destabilization of the n_S orbital, and stabilization of the n_A orbital. Although this is to be expected if through-space interaction is decreasing, the same behavior is observed for the $\phi = 0$ to $90°$ change for $\theta = 180°$, where through-space interaction is very small. The orbital energy changes observed as ϕ is varied are less than 0.2 eV in all cases, and the origin of this effect is not well understood.

Fixing ϕ at 0 or $180°$ and varying θ gave information on the extent of through-bond coupling in these species. For the (0,0) geometry, n_S is about 0.9 eV above n_A by EHT or ab ini-
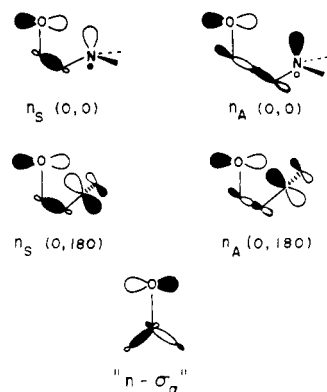
Figure 15. Schematic representation of the "symmetric" and "antisymmetric" nonbonding orbitals in α-amino ketones (Hoffmann) and in β,γ-unsaturated ketones (Houk). The "$n-\sigma_\alpha$" orbital is the delocalized n orbital found from semiempirical calculations.

tio methods, while at $90°$, this difference decreases to about 0.3 eV by EHT or 0.5 eV by ab initio methods. For the (180,180) geometry, the orbital separation is 1.2 eV (EHT) or 1.9 eV (ab initio). These results clearly indicate the strong conformational dependence of through-bond interactions and the relatively small magnitude of through-space interactions. This represents a major departure from the theoretical descriptions of β,γ-unsaturated ketones discussed earlier, because those treatments generally considered only through-space interactions.

The effect of varying the CCN angle was probed in both the (0,0) and (180,0) geometries. In the 0,0 geometry, the n_S over n_A order of levels is reversed at about $98°$, where an avoided crossing occurs. This is due to strong through-space interaction as $\angle CCN$ is decreased, and the n orbitals overlap more in space.

The influence of the σ^*_{CN} orbital on the π^*_{CO} orbital was also monitored by Hoffmann et al. as a function of geometrical changes. There was a slight lowering of the π^*_{CO} orbital energy for $\phi = 90°$, that is, where overlap of the π^*_{CO} and σ^*_{CN} orbitals is optimum.

Another interaction which was investigated, but was found to be small, was mixing of the nitrogen lone pair with the π system. This interaction had essentially no effect on the π_{CO} orbital, but destabilized the π^*_{CO} orbital in geometries where strong $n_N-\pi^*_{CO}$ interactions could occur.

These authors conclude that there is a maximum of 0.2–0.3 eV of through-space interaction between the lone pairs in the (0,0) or (0,180) geometries, while the through-bond interactions are larger and are maximum for $(\phi,0)$ and $(\phi,180)$ geometries.

Several examples are discussed where red shifts in α-amino ketones are attributed to lowering of π^*_{CO} by interaction with σ^*_{CN} and raising of the HO by n_O-n_N interaction. A "charge-transfer" transition is attributed to the $n_A \rightarrow \pi^*_{CO}$ excitation.

On the basis of these arguments, the following expectations for β,γ-unsaturated ketones are obtained. First, the most important ground-state interactions should be between the π_{CC} and n_O orbitals, which correspond to the n_N and n_O orbitals in Hoffmann's work, and the maximum interaction should occur for $(\phi,0)$ and $(\phi,180)$ conformations (through-bond) and (0,0) and (0,180) conformations (through-space). Since the π_{CC} orbital will often be at lower energy than a nitrogen lone pair, $\pi_{CC}-\pi_{CO}$ interactions can also occur, either through-space in the (90,0) and (90,180) geometries, or through bonds in planar conformations such as (0,90) or (180,90), mediated by the α-CH$_2$ pseudo-π orbital. Similar interactions between π^*_{CC} and π^*_{CO} should occur, but in light

of Hoffmann's calculations, little or no interaction between occupied and vacant orbitals should occur.

We have carried out calculations on β,γ-unsaturated carbonyl compounds in a number of geometries by the EHT, CNDO/2, and CNDO/S methods,[335,336] and the results of these calculations confirm the inferences drawn from the calculations of Hoffmann et al. and provide additional insight into orbital interactions and spectral properties of β,γ-unsaturated carbonyls. These results will be compared with experimental absorption and photoelectron spectra in the following sections.

Although irrelevant to ground-state orbital energies, tracing the energies of the two lowest vacant orbitals as a function of geometry gives insight into the extent of overlap possible between the two π systems. The extent of interaction is, of course, important in explaining spectral properties of these species. In the CNDO/S approximation, the extent of π^*_{CC} mixing with the π^*_{CO} orbital by a through-space mechanism varies from essentially 0 in the (0,180) geometry, where $\Delta\epsilon(\pi^*_{CO} - \pi^*_{CC}) = 0.13$ eV and the orbitals are unmixed, to 0.35 eV in the (90,180) geometry, where overlap is a maximum, $\Delta\epsilon$ is 0.82 eV, and each orbital mixes in 27% of the other. The (90,0) geometry, which could have additional overlap, has a splitting of only 0.83 eV, essentially identical with that of the (90,180) geometry. The implication is that qualitatively expected: $\pi-\pi$ overlap is a maximum when the p orbitals on C_1 and C_3 overlap most effectively. In the CNDO/S approximation, the π^*_{CC} and π^*_{CO} orbitals differ by only 0.13 eV when unmixed; the π_{CC} and π_{CO} orbitals differ by 2.8 eV in the (0,180) geometry, so that interaction of the occupied orbitals will be about 0.05 that of the vacant orbitals due to this difference, and even less because of the smaller coefficient on C_1 in the π_{CO} than in the π^*_{CO} orbital. In fact, CNDO/S, CNDO/2, and EHT calculations all indicate that the π_{CC} and π_{CO} orbitals do not mix to any appreciable extent.

The principal remaining interactions to be considered, and the only ones of importance in the ground-state, are the interactions between the n, π_{CC}, and σ orbitals of appropriate symmetry in the various geometries. From the results of Hoffmann, the through-space interactions of the π_{CC} and n orbitals should be small except at the (0,0) and (0,180) geometries, while through-bond interactions will be large at (ϕ,0) or (ϕ,180) geometries. The results obtained by CNDO/2, CNDO/S, and EHT methods are similar with the following exception: the CNDO/S and EHT calculations indicate that the n and π_{CC} orbital energies of 3-butenal are nearly degenerate in the noninteracting geometry (180,270), but the CNDO/2 calculations indicate that the n orbital is of considerably higher energy ($\sim$1.2 eV) than the π orbital. Since the ionization potentials of aldehydes are about 0.35 eV higher than those of the corresponding methyl ketones, and the n orbital in 3,3-dimethyl-4-penten-2-one is estimated to be 0.83 eV higher than the π orbital, the situation appears, in reality, to be somewhere between the CNDO/2 and CNDO/S calculations, but the n over π order seems reasonable for the β,γ-unsaturated ketones. Aside from this disagreement, the CNDO/2 and CNDO/S calculations do reveal the same type of interactions as geometries are varied. The fate of the n and π_{CC} orbitals is of some importance for both photoelectron spectral interpretations (vide infra) and for a clear identification of the nature of the enhanced $n\pi^*$ absorption. For (ϕ,270) or (ϕ,90) geometries, no interactions between n and π_{CC} orbitals occur. The n orbital is not completely localized but is mixed with the σ_{CC} and σ_{CH} orbitals in an antibonding fashion as it is in acetone or any other isolated carbonyl compound.[331,335] The π_{CC} orbital is mixed in an antibonding fashion with the appropriate σ_{CH_2} group orbital. As soon as the alkene is rotated toward $\theta = 0$ or 180°, a strong interaction of the π_{CC} orbitals with the remaining σ skeleton decreases, so that the n orbital energy

changes very little (the interaction with the π orbital is destabilizing, but the loss of hyperconjugation is stabilizing), while the π orbital is stabilized to a large extent (both the interactions with the n orbital and the loss of hyperconjugation are stabilizing). It is, therefore, unrealistic to neglect σ bonds, even those other than that connecting the carbonyl to C_α.

The CNDO/S method with configuration interaction was used to probe the energies and configurational compositions of the excited states. Since a molecular orbital method is used for ground-state calculations, delocalized ground-state orbitals are obtained, but configuration interaction is also considered in the calculation of transition energies and oscillator strengths. This semiempirical technique indicates that intensification of the $n\pi^*_{CO}$ transition in favorable geometries arises both from $n-\pi_{CC}$ and from $\pi^*_{CC}-\pi^*_{CO}$ interactions (before configuration interaction), which endows some $\pi_{CC}\pi^*_{CC}$ character on the $n\pi^*_{CO}$ transition, and from a significant contribution of the $\pi_{CC} \rightarrow \pi^*_{CO}$ "charge transfer" configuration to the lowest excited singlet ("$n\pi^*$") state. The second and third excited states consist of principally $\pi_{CC} \rightarrow \pi^*_{CC}$ or $\pi_{CC} \rightarrow \pi^*_{CO}$ configurations, although the relative energies of these two states are a rather sensitive function of geometry. The second excited singlet appears to generally be more accurately described as a $\pi_{CC}\pi^*_{CC}$ state, as suggested by Moscowitz, but does include significant contributions from $n\pi^*_{CO}$ and $\pi_{CC}\pi^*_{CO}$ configurations.

One important result of these calculations, which had apparently not been considered earlier, is the nature of the lowest triplet excited state of the β,γ-unsaturated carbonyls. CNDO/S calculations indicate that the lowest triplet state is invariably a $\pi_{CC} \rightarrow \pi^*_{CC}$ state, although in favorable geometries, $\pi_{CC} \rightarrow \pi^*_{CO}$ and $n \rightarrow \pi^*_{CC}$ configurations contribute to some extent. Only in completely noninteracting geometries, such as the (180,270), are the $\pi_{CC}\pi^*_{CC}$ triplet and $n\pi^*_{CO}$ triplet essentially isolated, noninteracting triplets. Only in such a case would discussions of intramolecular energy transfer, rather than internal conversion, be relevant to the actual photophysical processes occurring in β,γ-unsaturated carbonyls.

C. β,γ-Unsaturated Carbonyl Spectra

In this section, the experimental electronic, ORD–CD, and photoelectron spectra of β,γ-unsaturated carbonyls and the theoretical treatments presented in the previous section will be compared.

1. Absorption, ORD, and CD Spectra

a. β,γ-Unsaturated Carbonyls

Although the unusually intense $n\pi^*$ transitions around 290 nm in β,γ-unsaturated ketones had been noted previously, Cookson and Wariyar were the first to note the geometrical requirements and electronic factors required for this intensification.[327] Before any of the theoretical treatments appeared, these authors noted that in 63 β,γ-unsaturated and α-phenyl ketones available for comparison at that time, intensification was observed when the p orbitals of the carbonyl carbon and the alkene double bond pointed toward each other. In terms of the definitions given in Figure 12, these authors noted that intensification was greatest for the (90,0) or (90,180) geometries. Furthermore, Cookson and Wariyar noted that the intensification increased as the substitution of the double bond increased, indicating that the intensified transition was either of a charge-transfer type or simply an $n\pi^*$ transition intensified by some type of interaction with the alkene double bond. In Murrell's model, this would be due to the lowering of the $\pi_{CC}\pi^*_{CO}$ transition energy, so that it becomes closer in energy to, and mixes more efficiently with, the $n\pi^*_{CO}$ transition.

TABLE XXXIII. Summary of Uv Spectra of β,γ-Unsaturated Carbonyl Compounds (nπ* Transitions)

	λ_{max}, nm	ϵ	Approximate geometry[a]
Bicyclo[3.2.0]hept-6-en-2-ones (Table I)	303–319	100–460	(60,150)
Bicyclo[4.2.0]oct-7-en-2-ones (Table II)	296	85–168	(60,150)
Bicyclo[3.2.0]hept-2-en-7-ones (Table III)	302–331	160–289[b]	(60,150)
Bicyclo[2.2.1]hept-5-en-2-ones (Table IV)	303–318	250–485[b]	(110,200)
Bicyclo[4.2.0]hept-2-en-8-ones (Table VII)	311	156	(60,150)
Bicyclo[2.2.2]oct-5-en-2-ones (Table VIII)	293–300	107–433	(120,210)
Bicyclo[3.n.1]alkan-2-en-(6 + n)-ones (Table IX)	290–299	45–180	(110,240)
3-Cyclohexenones (Table XII)	275–285[c]	19–70[b]	(150,270)
3-Cycloheptenones (Table XII)	282–292	41–460	(90–150, 210–330)
2-Alkenylcyclopentenones (Table XI)	290–310	28–110	(60,θ)[c]
3-Cycloalkenones (ring n > 7) (Table XIII)	287–292	47–67	(ϕ,θ)[c]
2-Alkenylcycloalkanones (ring n > 5) (Table XIII)	290–298	20–292	(ϕ,θ)[c]
3-Methylenecyclobutanone (Table XIV)	293	22	(180,90)
3-Alkylidenecyclohexanones (Table XIV)			
Acyclic	293–299	35–121	(130,50)
2,4-Bridged-3-alkylidenecyclohexanones	286–298	58–304	(120,30) or (180,30)
Acyclic β,γ-unsaturated ketones (Table XVI)	280–296	32–164	(ϕ,θ)[c]
Acetonylcycloalkenes (Table XVIII)	288–302	106–151	(ϕ,θ)[c]
Acylcycloalkenes (Table XVIII)	288–300	82–151	(ϕ,30)[c]
3-Cyclopentenones (Table XIX)	300–313	7–11	(180,270)
7-Norbornenones (Table XIX)	270–274	21–58	(120,240)
α,β,β',γ'-Unsaturated ketones (Table XIX)	320–337	33–560	(ϕ,θ)[c]
δ-Keto-β,γ-unsaturated ketones (Table XXI)	293–349	33–560	(ϕ,θ)[c]
β,γ,δ,ε-Unsaturated ketones (Table XXII)	275–285	150–2500	(ϕ,θ)[c]
3,5-Cycloheptadienones (Table XXIII)			
Monocyclic (C_2 assumed)	278–290	602–710	(150,210)
2,7-Bridged	269–292	460–4010	(90,330)
β,γ-Unsaturated aldehydes (Table XXIV)			
3-Formylcycloalkenes	302–308	103–135	(ϕ,130)[c]
2-Formylalkylidenecycloalkenes	297–302	10–71	(ϕ,30–330)[c]
Enol esters (Table XXV)	238	20,500	(ϕ,θ)[c]
β-Diketones (Table XXVI)	224–244	218–535	(~150,~60)
	281–303	50–162	
α-Aryl ketones (Table XXIX)	283–298	50–314	(ϕ,θ)[c]
α-Aryl aldehydes (Table XXX)	297–303	106–301	(ϕ,θ)[c]
Aryl esters (Table XXXI)	259	230	(ϕ,θ)[c]

[a] The enantiomer with smallest positive angles (Figure 12) is listed. The geometries were estimated from models. [b] Only those compounds without additional chromophores are included in these ranges. [c] Unspecified angle implies that the molecule is not conformationally rigid.

The Labhart and Wagniere or Moscowitz models account for this phenomenon in a similar way, since alkyl substitution lowers the alkene ππ* transition energy.

Cookson and Wariyar also noted that the compounds which showed the largest intensifications also had very large optical rotations and Cotton effects. The work of Cookson and Wariyar prompted much of the subsequent spectroscopic and theoretical work on β,γ-unsaturated ketones.

In the spirit of Cookson and Wariyar's table which includes spectroscopic data on 63 β,γ-unsaturated carbonyl compounds, Table XXXIII lists generalized spectroscopic data for the different types of compounds discussed in the first section of the review. For the absorption spectra of particular types of compounds, the reader is referred to the individual tables in earlier sections and to Cookson and Wariyar's paper.[327]

Although the spread in nπ* extinction coefficients is quite large, the general trend of increasing ϵ with increasing $|\sin \phi|$ and $|\cos \theta|$ is observed, although qualitatively, the $|\cos \theta|$ dependence seems of more importance than the $|\sin \phi|$, as would be expected for predominant through-bond coupling.
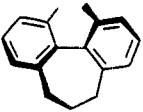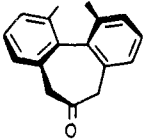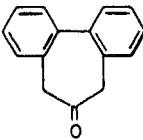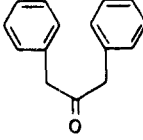
The profound influence of β,γ-unsaturation upon the magnitude of Cotton effects in inherently dissymmetric carbonyl compounds was discovered by Mislow et al.[338] These authors investigated the ORD spectra of a number of acetone-bridged biphenyls. The overlap of the carbonyl n and benzene π orbitals resulted in enhanced nπ* absorption and an unusually large amplitude of the Cotton effect at about 300 nm which dominates the ORD spectrum. The ultraviolet and partial ORD spectra of two of these compounds, along with the corresponding noncarbonyl and acyclic dibenzyl ketone analogs are given in Table XXXIV.[338] Mislow et al. noted that the exaltation of the nπ* maximum required overlap of the aromatic π orbitals and the carbonyl n orbitals, and that the sign of the Cotton effect was diagnostic of the sense of chirality of the α-phenyl ketone chromophore.

A detailed analysis of the β,γ-unsaturated carbonyl chromophore was carried out by Moscowitz et al. in a paper which also contained the theoretical treatment referred to earlier.[232] Empirically, the large amplitudes of the Cotton effects in β,γ-unsaturated ketones were found to be typical of those compounds approximating the (90,180) geometry. Furthermore, those species with a geometry approximating (90,180) exhibit large negative Cotton effects, while those with the enantiomeric (270,0) geometries display large positive Cotton effects. The (90,180) and (270,0) geometries place the alkene in the back upper right and the back lower right octants, respectively, and the location of the double bond in this inherently dissymmetric chromophore overrides the influence of alkyl substituents in other octants. That is, two very different β,γ-unsaturated ketones such as dimethyl-suberone and parasantonide have nearly identical ORD spectra because the extended chromophores have similar geometries in the two molecules.[317]

Recently, Wagniere and Hug proposed a simple model for

TABLE XXXIV. Ultraviolet Spectra of Acetone-Bridged Biphenyls (Isooctane)[338]

Compound	λ_{max}, nm (ϵ)	nπ^*	ORD
	240(11500), sh274(700)		$[\alpha]_{254} = -20,200°$ $[\alpha]_{230} = +38,108$
	245(9770), sh272(14800)	289.5(759), 297.5(759), 307(575), 317(257)	$[\alpha]_{310} = -28,000°$ $[\alpha]_{284} = -133,450$
	249.5(15850)	sh287.5(759), 296(646), 305(437), 316(174)	
	244(170), sh249(234), 254.5(324), 259.5(398), 266(339)	sh287(214), 294(234), sh302(224), sh311(162), sh322(646)	

predictions of the signs of the Cotton effect in molecules of effective C_2 symmetry.[339] Applications to dimethylsuberone (the second entry in Table XXXIV) led to the prediction of a negative Cotton effect for the molecule of right-handed chirality, as is observed. The simple model indicates that transitions of A (in C_2) symmetry will display negative Cotton effects for a chromophore of right-handed chirality, while B transitions will display positive Cotton effects in a right-handed chromophore. The nπ^* transition is of A symmetry, so that a rule identical with the generalized octant rule emerges for β,γ-unsaturated carbonyl compounds.

Mislow and Berger prepared optically active 2-norbornenone and bicyclo[2.2.2]oct-5-en-2-one of known configurations and found that these compounds, which have approximately (270,0) geometries, both have large positive Cotton effects for the nπ^* transitions.[340] The CD spectra of several β,γ-unsaturated ketones were reported by Bunnenberg et al., who found that the CD and nπ^* absorption curves correspond quite closely, with the sign of the CD curves corresponding to the generalized octant rule derived for ORD spectra.[333]

Ultraviolet and CD studies of several β,γ-unsaturated acetyl steroids were used by Gorodetsky et al. to establish the configurations and conformations of these systems.[341] Whereas the equatorial epimer 451b exhibits a weak nπ^* transition [λ_{max}(cyclohexane) 286 nm(ϵ 38)] and a small positive ($\Delta\epsilon_{292}$ = +1.68) CD maximum, the axial epimer 451a has a red shifted and enhanced nπ^* absorption [λ_{max}(cyclohexane) 283(195), 291(130), 299(137), 310(109), sh 320(53)], a detectable short wavelength shoulder [202(500)], and a large negative maximum ($\Delta\epsilon_{297}$ = −11.71) in the CD spectrum. The conformations 453 and 454 were deduced for 451a and 451b, respectively, from these data. The conformation 453 has approximately a (90,270) geometry, which places the double bond in the back left octant, but μ_e (CC) will be approximately perpendicular to μ_m (CO). The boat conformation, 454, proposed for 451a by Gorodetsky et al., has approximately a (90,240) geometry, and although a negative rotation is expected for such a conformation since the alkene is in the back upper right octant, μ_e and μ_m will be nearly perpendicular. An alternative chair conformation, resembling 453 but with an axial acetyl group (also rotated by 180°), will have a (90,180) geometry, ideal for a large negative CD maximum. The conformation 454 proposed by Gorodetsky might have a

large negative CD if the acetyl were rotated by 180°. This would produce an alignment of μ_e and μ_m and might place the alkene in the front upper left octant.

451

452

453

454
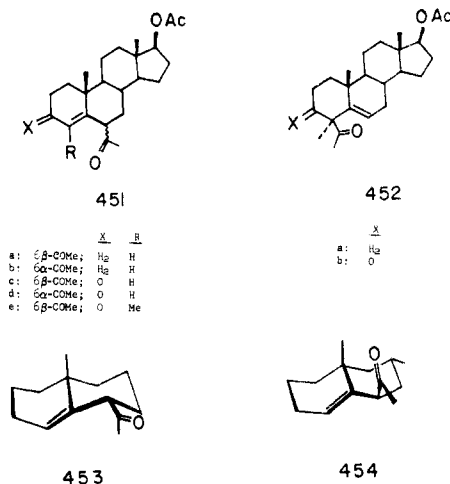
Compound 452a gives a large positive CD maximum ($\Delta\epsilon_{298}$ = +11.32) so that the chiral β,γ-unsaturated ketone chromophore is enantiomeric to that of 451a. This pair provides another dramatic example of the dominating influence of the double bond on determining not only the sign, but also the magnitude of the CD maxima. The ultraviolet absorption spectrum [λ_{max} (cyclohexane) sh 283 (72), 293 (90), 299 (102), 309 (72), sh 320 (38)] also shows the coupling of the carbonyl and alkene functions.

The β,γ-unsaturated β'-diketone 452b has a moderately enhanced nπ^* absorption [λ_{max}(cyclohexane) 291 nm (149)], but has a relatively low positive maximum ($\Delta\epsilon_{309}$ = +3.31) in the CD spectrum indicating a geometry unsuitable for substantial interaction. The δ-keto-β,γ-unsaturated ketone 451d has a small negative CD maximum ($\Delta\epsilon_{340}$ = −1.3) and no enhanced nπ^* absorption, indicating a conformation akin to 453. The 6β-analogs 451c and 451e have enhanced nπ^* absorptions and large negative CD maxima ($\Delta\epsilon_{297}$ = −27.0) indicating that both of these molecules possess conformations similar to 454,[341] or the alternatives proposed here.

Gorodetsky and coworkers made further conclusions about the conformations of steroidal 5-en-3-ones.[342] Cholest-5-en-

3-one (**455a**) has an nπ* absorption [λmax (C6H12) 297 nm (ε 55)] which is weaker than those of bicyclic systems or of **451a**, but is stronger than that of the saturated analog **456a** [λmax (C6H12) 288 nm (ε 14)].[342] The CD spectrum of **455a** (Δε290 = +2.9) has a larger amplitude than does that of **456a** (Δε295 = 1.2), and this and the structured nπ* absorption of **455a** as compared with the broad maximum for **456a** indicate that coupling of the alkene and carbonyl groups occurs to some extent in the former. The geometry (240,120) is compatible with this expectation. Similarly the nπ* absorption maxima of **455b** [λmax (C6H12) 263 nm (ε 63)] and **455c** [λmax (C6H12) 296 nm (ε 75)], the vibrational structure of these bands, and the CT bands at 210 nm indicate coupling of chromophores in the compounds. For **455a–c**, the chair conformations **457** were proposed.[342]

455   **456**

R1	R2	R3	R4
a:	H	H	Me	-C8H17
b:	H	H	H	OAc
c:	Me	Me	H	OAc
d:	Me	Me	Me	-C8H17
e:	Et	Et	Me	OAc

457   **458**
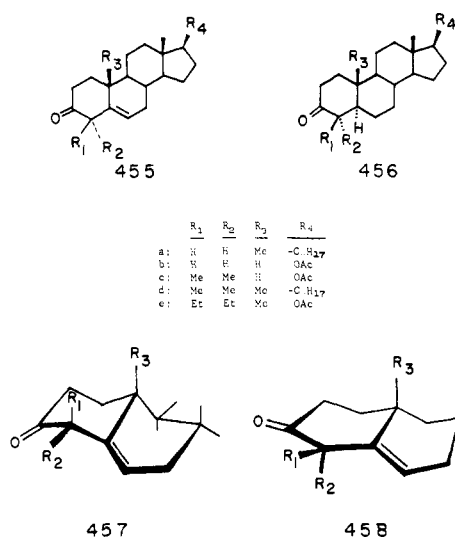
The absorption spectra of the trimethyl (**455d**) and the diethylmethyl (**455e**) analogs do not have enhanced nπ* absorption. The spectra of **455d** [λmax (C6H12) 293 nm (ε 32)] and **455e** [λmax (C6H12) 296 nm (ε 36)] differ only slightly from that of the saturated analog **456d** [λmax (C6H12) 295 nm (ε 18)]. Only small differences in the CD spectra of the unsaturated and saturated compounds are noted. Steric repulsions between the axial 4-alkyl group and the 19-methyl are believed to cause distortion toward a boat ring A as shown in **458**. This geometry (~130,130) allows very little overlap of the πcc and πco orbitals.[342]

MacKenzie and coworkers[343,344] attempted to distinguish between Cookson's model for nπ* enhancement which assumed that intensification was proportional to overlap of the πcc and πco orbitals,[327] and Labhart and Wagniere's[326] which suggested that overlap of n and πcc orbitals and a strong CT band (requiring πcc and πco overlap) was necessary. For α-phenyl ketones, better agreement of Cookson's formulation was found, but the result was interpreted as meaning only that the geometry proposed by Cookson (90,0), or (90,270) was required for intensification, and no interpretation of which interaction was more important could be made.

The MacKenzie treatment, in which conformer populations based on a molecular mechanical model, overlap in each conformation, and an average nπ* exaltation based on various models of enhancement are calculated, was extended to substituted phenylacetones.[345-347] This work was interpreted as supporting the Cookson proposal—that only πco overlap with πcc, and not n with πcc, was important.

Bays, Cookson, and MacKenzie reported the ultraviolet and CD spectra of a number of bornenones[348] in connection with photochemical studies of these systems. They found both strongly enhanced nπ* absorptions and shorter wavelength

ππ* transitions, and several observations were consistent with the "coupled oscillator" or configuration interaction model for these transitions. First, in the series of phenylbor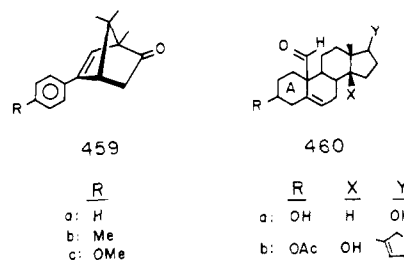nenones **459a–c**, the intensity of the nπ* band increases [λmax (C6H12) nm (ε) 318 (6170) for **459a**, 315 (6250) for **459b**, 318 (7570) for **459c**], and, while the ππ* band intensi-

459   **460**

	R
a:	H
b:	Me
c:	OMe

	R	X	Y
a:	OH	H	OH
b:	OAc	OH	

ty increases also [265 (15400), 266 (16100), and 272 sh (17400) respectively], this increase is less than for the corresponding deoxo analogs.[348] Thus, the intensity gained by the nπ* transition is lost by the ππ* transition. Secondly, the signs of the Δε's for the nπ* and ππ* CD are opposite, and the magnitudes are nearly the same. Third, as the ππ* transition energy decreases in the series **459a–c**, the nπ* enhancement increases, compatible with stronger coupling as the energies of the coupled transitions become more nearly the same.[348]

A number of other β,γ-unsaturated ketones were investigated, and the signs of the CD Δε's were found to agree with the generalized octant rule. Of particular interest, the β,γ-unsaturated aldehydes **460a** and **b** were both found to have negative long wavelength CD maxima (Δε310 = −8.05 and Δε310 = −7.0, respectively), compatible only with conformations in which the double bond is in the upper right back octant, which requires that the carbonyl oxygen be over ring A.[348] If the CO bond were aligned along the 5–10 bond of the steroid system, the double bond would be in the lower *front* right octant, also compatible with a negative CD maximum.

Several other CD or ORD spectra of β,γ-unsaturated carbonyls have been reported, although the conformations of these systems have not been discussed in the literature. Nakanishi et al. reported a moderate negative CD for **135b** (Δε300 = −2.4).[86] The chiral chromophore of this system is approximately enantiomeric to that in **455b** (Δε295 = +1.2)[86] compatible with the (180,150) geometry of this species.

Seeman and Ziffer reported the CD spectra of the 5-vinyl-norsteroids for which they reported stereospecific 1,2-shifts. The 5β-vinyl compound, β-vinyl-**95a**, has a larger positive CD maximum (Δε300 = +3.03) than the corresponding 5β-ethyl compound (Δε305 = +0.79).[56] The positive rotation suggests that the 5-substituent is located in the upper right *front* octant, which is also the geometry required to explain the stereochemistry of the 1,2-shift. The 5α-vinyl-**95a** has a moderate negative CD (Δε = −4.06)[56] indicating the vinyl is in the lower right *front* octant.

b. Related α-Heterosubstituted Carbonyls

Although not related to the β,γ-unsaturated ketones in terms of photochemistry, α-hetero ketone spectra are closely related to β,γ-unsaturated ketone spectra. Perhaps the earliest known and most thoroughly studied examples of these types of compounds are the α-halo ketones. Although the literature will not be reviewed here, a summary of the data leads to further insight into the generality of the types of interactions present in β,γ-unsaturated ketones.

The ultraviolet spectra and ORD and CD spectra of axial 2-halo ketones and equatorial 2-halo ketones are significantly different.[349,350] The nπ* absorptions of the equatorial 2-halo-

cyclohexanones are shifted 4–7 nm (F, Cl, Br) to longer wavelengths than those of the corresponding cyclohexanones, and the ORD peaks are shifted to longer wavelengths, but to a smaller extent. An equatorial halogen has a small effect on the ORD amplitude, compatible with the location of halogen in the carbonyl plane. Alternatively, we may relate this geometry to the ϕ,θ definitions by noting that $\phi \simeq 10°$ for an equatorial halogen, while θ vanishes for the cylindrically symmetrical halogen.

Axial 2-halogens cause a long wavelength shift of the absorption maxima (~12 nm for F to ~24 nm for Br) and an enhancement of the $n\pi^*$ absorption intensity (~20 for F to ~120 for Br). The ORD maxima also shift [20 ± 5 nm (F, Cl, Br) or 32 nm (I)] to longer wavelength upon axial halogen substitution. The rotatory dispersion amplitudes of the axial 2-halo ketones are enhanced 10–20-fold over those of the ketone or equatorial halo ketones, and a 2-axial chlorine or bromine dominates the sign of the Cotton effect, in the same fashion that a β,γ-double bond does. These phenomena have been generalized as the "axial-halo ketone rule".[349] Axial 2-halo ketones have $\phi \simeq 130°$, so the generalizations about β,γ-unsaturated carbonyls apply to the α-halocarbonyls also.

Allinger et al. applied molecular orbital methods to the study of the red-shift induced by axial halogens and concluded that the phenomenon was a result of the mixing of the π^*_{CO} level with a low-lying σ^*_{CX} orbital.[350] This can occur for ϕ near 90°, but not for ϕ near 0°. Allinger et al. proposed that a similar phenomenon will occur whenever a suitably disposed sufficiently "weak" bond or CX bond with a low-lying vacant orbital is available to mix with the π^*_{CO} orbital.[350]

Similar arguments, combined with n_O, n_N mixing, emerge from the α-amino ketone calculations by Hoffmann et al.[325] Both enhanced $n\pi^*$ transitions and "charge-transfer" bands have been noted in a variety of α-amino ketones,[351] α-mercapto ketones,[352] α-cyclopropyl ketones,[353] and α-alkoxy ketones.[354] The last study cited also reports a comparison of uv and CD spectra of 3-aza, thia-, and oxacyclohexanes.[354] In light of Moscowitz's coupled oscillator study of β,γ-unsaturated ketones, it might be prudent also to consider the possibility that these transitions could result from coupled $n\pi^*_{CO}$ and $n_X\sigma^*_{CX}$ transitions.

Whatever the most accurate description, it appears that the "charge-transfer" and enhanced $n\pi^*$ absorptions observed in β,γ-unsaturated carbonyls are but one, particularly dramatic, example of a general phenomenon, observable whenever a carbonyl group and a group of low ionization potential are present in a molecule with the proper mutual geometrical disposition.

c. "σ-Coupled" Transitions in γ,δ-Unsaturated Ketones

Stretching the generality of spectroscopic phenomena in β,γ-unsaturated ketones even further, γ,δ-unsaturated ketones with particular geometries exhibit enhanced $n\pi^*$ and so-called "σ-coupled" or charge-transfer transitions not unlike those in β,γ-unsaturated ketones.

Winstein, DeVries, and Orloski reported the synthesis of several polycyclic 4-methylenecyclohexanones held in boat conformations.[355] These materials all have absorptions at 210–239 nm (ϵ 3000–4000) in heptane and at 214–244 nm (ϵ 1500–2500) in ethanol, characterized as charge transfer ($\pi_{CC}\pi^*_{CO}$) transitions. The $n\pi^*$ absorptions were not enhanced, since the n and π_{CC} orbitals cannot interact owing to their opposite symmetries.[357]

Cookson et al. discovered that molecules with the **461** carbon skeleton have moderate intensity bands around 224 nm which are absent in the endo analogs **462**. Furthermore, molecules such as exo-**461** have $n\pi^*$ transitions with about twice the intensity of those in endo-**462**. The large hypso-

461   462

463   464
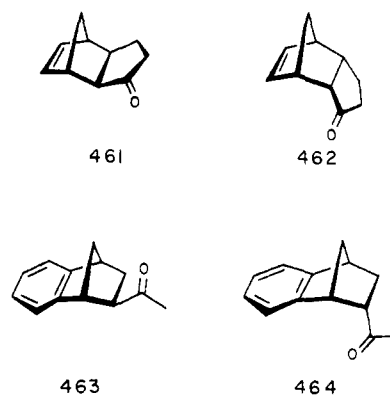
chromic shift of the 224-nm band upon changing from ethanol to hexane solvent led to the suggestion that this band was an intramolecular charge-transfer band, which appears only when the overlap of the π_{CC} and π_{CO} orbitals with the intervening σ orbitals is large.[356] The photoelectron spectra of these systems,[357] discussed in the following section, shed further light on the types of orbital interactions which occur in these molecules.

Calculations which we have performed by CNDO/2 and CNDO/S methods[358] reproduce the greater orbital interactions in models approximating exo-**461** than in those like endo-**462**. Both the n-π_{CC} and the π^*_{CC}-π^*_{CO} interactions are greater in the exo models than in the endo models, and the difference arises from more favorable through-bond interaction in the exo geometry than in the endo geometry. The enhanced and red-shifted $n\pi^*$ transition is a direct consequence of the interaction of the two chromophores. In terms of a Labhart–Wagnieré-type model, the mixing of the n and π_{CC} orbitals removes some of the forbiddenness of the $n\pi^*_{CO}$ transition, while in Murrell or Moscowitz models, the $n\pi^*_{CO}$ transition borrows intensity from the $\pi_{CC}\pi^*_{CO}$ transition and the $\pi_{CC}\pi^*_{CC}$ transitions in the exo geometry, but not in the endo geometry.

The photochemistry of γ,δ-unsaturated ketones is quite markedly affected by the geometry of the system. Observations by a number of groups are referred to in ref 359. The absorption spectra and the photochemistry of the 2-acetylbenzonorbornenes are quite different depending on the exo or endo nature of the acetyl group.[359] Thus, the exo compound **463** has an enhanced $n\pi^*$ absorption [λ_{max} 293 nm (ϵ 77)], and gives α-cleavage as well as efficient intersystem crossing [Φ_{isc} = 0.83] upon photolysis. The endo epimer **464** has a normal $n\pi^*$ transition [λ_{max} 293 nm (ϵ 28)], is photochemically unreactive, and intersystem crossing occurs inefficiently [Φ_{isc} = 0.20]. Sauers and De Paolis proposed that the $n\pi^*$ singlet of the exo compound behaves normally, while the $n\pi^*$ singlet of the endo compound is unusual, in that some deactivation pathway competes effectively with intersystem crossing.[359] By analogy to earlier suggestions, a singlet intramolecular exciplex is suggested to account for the enhanced internal conversion of the $n\pi^*$ singlet to ground state.[359]

An alternative suggestion is that the endo compound is normal, while α-cleavage and intersystem crossing are accelerated in the exo compound by the same mechanism that causes the enhancement of the $n\pi^*$ transition intensity. Perhaps a hybrid of these two suggestions is required to explain the experimental results.

Studies of rigid polycyclic β-amino ketones have led to conclusions similar to those for γ,δ-unsaturated ketones. Hudec[351] concluded that intensification and red shifting of the $n\pi^*$ transition in β-amino ketones occurred if the nitrogen lone-pair were anti-periplanar to the C_α-C_β bond, and in such compounds, a new "charge-transfer" band appears at 220–240 nm. This band may, alternatively, be described as part of

a split $\pi\pi^*$ transition. A number of interactions were postulated on empirical grounds, such as $\sigma^*_{CN}-\pi^*_{CO}$ and $n_N-\pi_{CO}$, as well as the n_N-n_O interaction favored by the anti-periplanar arrangement of the nitrogen lone pair and the $C_\alpha-C_\beta$ bond.[351]

Fluorescence studies on β-amino ketones in different solvents indicate a very high dipole moment for the singlet excited states, suggesting considerable charge transfer of the $n_N \rightarrow \pi^*_{CO}$ type.[360]

The interaction of carbonyl and alkene orbitals or transitions can be observed in even more remotely situated chromophores. For example, Leonard and Owens found that the $n\pi^*$ transition in trans-5-cyclodecenone [λ_{max} 302 nm (ϵ 73)] was about five times more intense than that in cyclodecanone, and the position of the $n\pi^*$ λ_{max} was solvent insensitive.[361] A new band [λ_{max} (C_6H_{12}) 260 nm (ϵ 423)] was also observed in the unsaturated ketone, suggesting some type of alkene–carbonyl interaction. This band shifted slightly to longer wavelength in polar solvents.[361]

Kosower and coworkers called the short wavelength transition around 200 nm in trans-5-cyclodecenone[λ_{max} (i-C_8H_{18}) 188 nm (ϵ 8700)] a "photodesmotic transition", since they believed that a partial bond between the carbonyl and the alkene was formed in the excited state.[362] This transition shifted to longer wavelength with increasing solvent polarity. The $n\pi^*$ transition of this compound was reported to be weak [λ_{max} (i-C_8H_{18}) 279 nm (ϵ 18)] and shifted to shorter wavelengths in polar solvents without a change in intensity. The 6-methyl derivative showed similar behavior.[363]

In summary, interactions between alkene (or lone pairs) and carbonyl chromophores are by no means restricted to β,γ-unsaturated carbonyl compounds, but as the separation the chromophores increases, the geometrical requirements for through-bond and through-space interactions become more demanding.

2. Emission Spectra

Only limited data on β,γ-unsaturated carbonyl emission spectra are available. Schaffner and coworkers reported observations of phosphorescences in several δ-keto-β,γ-unsaturated ketones and aldehydes.[178,364] These phosphorescences were similar to those observed from $\pi\pi^*$ triplets of the corresponding α,β-unsaturated ketones and aldehydes. For the steroid system 256a, the quantum yield of phosphorescence was quite high at 77°K (Φ_p = 0.43 ± 0.15), nearly double that of simpler α,β-unsaturated ketone analogs. The triplet lifetime (32 msec) is indicative of a $^3\pi,\pi^*$ state which must lie only a few kcal/mol below the $^3n,\pi^*$ state. The photochemistry of δ-keto-β,γ-unsaturated ketones such as 256a
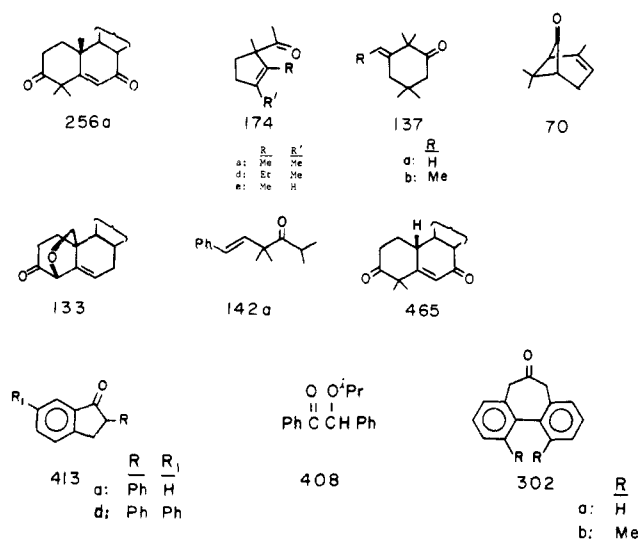
TABLE XXXV. Triplet Energies and Lifetimes of β,γ-Unsaturated Carbonyls Obtained from Phosphorescence Data

Compound	Triplet energy (± 1.5 kcal/mol)[a]	Mean life time, msec	Ref
174a	<78	80.5	114
174d	70	165	114
174e	~74	43	114
256a	68.9	23 (32)	365
324a	71.5	28	235
137a	70.7	205	365
137b	68.9	156	365
2-Norbornenone	69.5	190	365
3-Cyclooctenone	68.4	95	365
2,2-Dimethyl-3-cycloheptenone	68.6	44	365
Chrysanthenone (70)	69.2	34	365
142a	68.6	49	365
133	73.7	55	365
465	68.9	48	365
Benzobicyclo-[2.2.2]octadienone	60.9	210	365
413a	74	1	365
413d	66	5500	365
408	73.4	30	365
204a	74	5.5	133
204b	70	105	133
267a	$\gtrsim 60$[b]	5.5	186
267b	$\gtrsim 60$[b]	3.4	186

[a] From 0–0 phosphorescence band at 77°K in EtOH or isopentane. [b] Only λ_{max} reported.

is compatible with these observations, since these compounds undergo oxa-di-π-methane rearrangements from triplet states formed by efficient intersystem crossing of the α,β-unsaturated ketone.

Schaffner and Gonzenbach[114] have observed phosphorescences from the simple β,γ-unsaturated ketones 174a, d, and e, indicative of $\pi\pi^*$ triplet states, and Hancock and Grider have reported phosphorescences from a large variety of β,γ-unsaturated ketones at 77°K.[365] These results are recorded in Table XXXV. Hancock and Grider conclude that $\pi\pi^*$ triplet states emit in these compounds on the basis of lifetimes, vibrational spacings, and small shifts (2-5 nm) to longer wavelength of the 0-0 band when ethanol replaces isopentane as solvent. Only 256a has a sufficiently short lifetime to suggest a possible $^3n\pi^*$ state, while the triplet lifetime of 3-cyclooctenone decreased to 5.4 msec in isopentane, suggesting a possible inversion of triplet state ordering from that in ethanol. It is surprising that these compounds phosphoresce, since the triplet-sensitized photochemistry of these compounds is entirely different from that observed upon direct irradiation, suggesting very inefficient intersystem crossing at best. Furthermore, Engel and coworkers have attempted to observe phosphorescences from a number of simple β,γ-unsaturated ketones, but have invariably failed to observe emission of any type attributable to the β,γ-unsaturated ketones.[366] The question of whether nonconjugated β,γ-unsaturated ketones emit does not seem entirely resolved.

In late 1974, Schexnayder and Engel reported convincing evidence that neither 2-norbornenone nor 80a, a compound known to intersystem cross, phosphoresces, and that the triplet energies of simple β,γ-unsaturated ketones are about 76 kcal/mol,[18a] significantly above those energies (~69 kcal/ mol) claimed by Hancock on the basis of 0-0 energies in the phosphorescence spectra. We are forced to conclude that the only β,γ-unsaturated ketones for which authentic phosphorescence data have been reported are those compounds
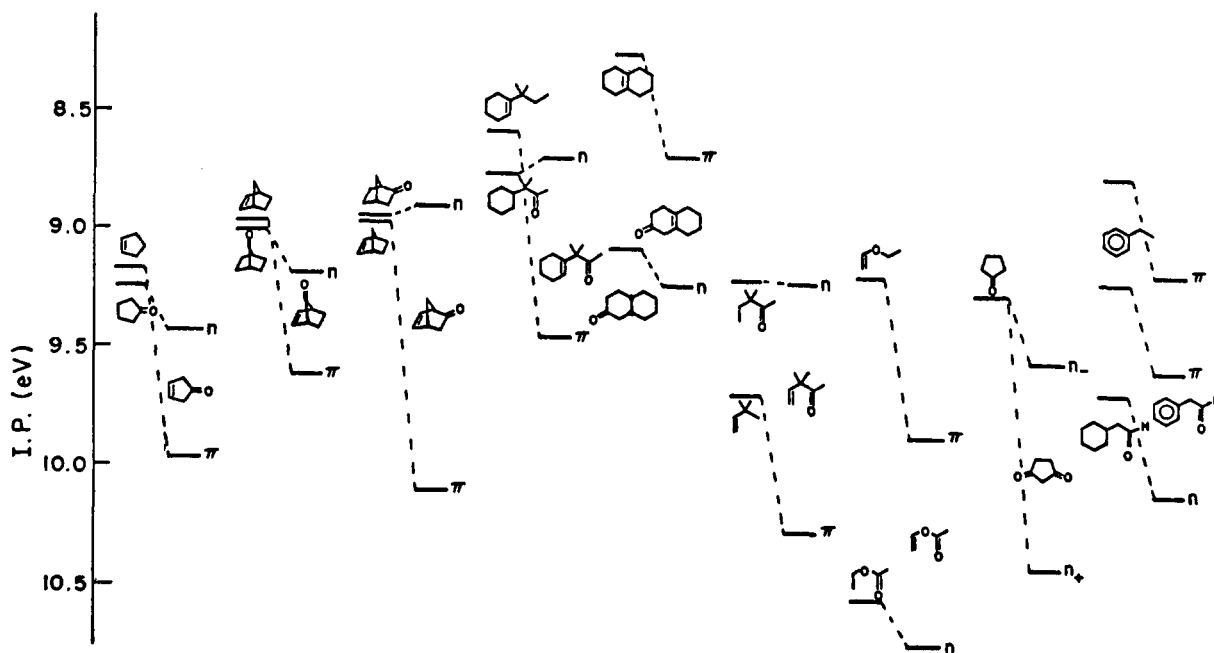
Figure 16. Ionization potentials of β,γ-unsaturated carbonyl compounds and corresponding monochromophoric models. The following ionization potentials were estimated: ethyl vinyl ether from n-butyl vinyl ether (9.08 eV); ethyl acetate from methyl acetate (10.59 eV); ethylbenzene from toluene (8.82, 9.20 eV); cyclohexylacetaldehyde from isobutyraldehyde (9.69 eV).

which are simultaneously α,β-unsaturated ketones.

The phosphorescences from several $\alpha,\beta,\beta',\gamma'$-unsaturated ketones, which are expected to intersystem cross efficiently, have been reported. The indanone, **413a**, is reported to have a lowest $n\pi^*$ triplet (E_T = 74 kcal/mol; τ = 1 msec). Whereas **413a** undergoes a facile photochemical α-cleavage, the unreactive **413d** has a lowest $\pi\pi^*$ triplet (E_T = 66 kcal/mol, τ = 5.5 sec).[292] The benzoin ether **408** has a lowest $n\pi^*$ triplet (E_T = 73.4 kcal/mol; τ = 30 msec) and undergoes the α-cleavage reaction efficiently.[292]

The 3-benzoylcyclopentenes **204a** and **204b**, which undergo triplet α-cleavages and 1,3-shifts, are found to have lowest $n\pi^*$ triplet states from phosphorescence studies (Table XXXV).[133] Similarly, deoxybenzoins phosphoresce from $n\pi^*$ states and undergo α-cleavage reactions.[293]

The dibenzocycloheptadienones **302** and their deoxo analogs exhibit two emissions at both 77°K and at room temperature in fluid solution.[367] The two emissions resemble closely the $\pi\pi^*$ fluorescence and phosphorescence bands of biphenyl at 77°K. However, both emissions persist at room temperature in fluid solution in **302**, whereas the phosphorescence of biphenyl is not observed under these conditions. Wahl and coworkers assigned the shorter wavelength emission at 320 nm (89.2 kcal/mol) in **302** to $\pi\pi^*$ fluorescence. The longer wavelength emission of **302a** (454 nm in alcohol at 77°K; 464 nm in alkane glass at 77°K, τ = 3.11 sec) was assigned to $\pi\pi^*$ phosphorescence. This assignment was supported by esr studies. Some type of $n\pi^*$ mixing with the $\pi\pi^*$ state was considered a possible source of this unusual phosphorescence in fluid media.[367]

Schuster, Kim, and Knudsen have observed broad featureless emissions at 410–430 nm from several 3,5-cycloheptadienones at room temperature in fluid solution. The failure of oxygen to quench these emissions suggests that the emissions are fluorescences from lowest $n\pi^*$ singlet states.[210] The measurement of singlet lifetimes, now in progress, will allow quantitative tests of the mechanistic postulates made for the systems.

3. Photoelectron Spectra

Photoelectron (PE) spectra of several series of β,γ-unsatu-

rated carbonyls and related compounds have been reported. Assuming Koopmans' theorem,[368] ionization potentials can be equated to the negatives of SCF orbital energies and can, therefore, give information about orbital interactions in the ground states of molecules. The reported data are collected in Table XXXVI. Figure 16 shows the n and π vertical ionization potentials (I_v's) of several types of β,γ-unsaturated carbonyl systems along with the I_v's of appropriate model systems.

The separation of orbital energy changes into those due to "inductive effects" (of various types), n–π_{CC} interactions, and π_{CC}–π^*_{CO} interactions, and the magnitude of carbonyl inductive effects have been estimated variously by different authors.

Chadwick, Frost, and Weiler reported the PE spectra of 3-cyclopentenone,[369] 2-norbornenone,[369] and 7-norbornenone.[370] As shown in Figure 16, the carbonyl n orbital energies are lowered by 0.19 and 0.18 eV in 3-cyclopentenone and 7-norbornenone as compared to the saturated analogs, and this was attributed to the inductive effect of the alkene. The 0.80 and 0.67 eV lowering of the alkene orbital energies in 3-cyclopentenone and 7-norbornenone was dissected into a carbonyl inductive effect, and 0.56 and 0.4 eV lowerings due to π_{CC}–π^*_{CO} interactions. The latter interaction would destabilize the π^*_{CO} orbital. The lowering of the n orbital energy and the raising of the π^*_{CO} orbital energy is said to account for the difference in $n\pi^*$ transition energies in 7-norbornanone (4.25 eV) and 7-norbornenone (4.53 eV).[370]

While the compounds mentioned in the previous paragraph cannot have n–π_{CC} interactions for symmetry reasons, 2-norbornenone can have these interactions, as was discussed in detail earlier. The PE spectrum clearly reveals this, since the n orbital energy is 0.04 eV higher than that of 2-norbornanone. Correcting for inductive effects, a 0.24-eV n–π_{CC} interaction is deduced. Assuming this and the usual inductive effect lowering the π_{CC} energy, a net 0.81-eV π_{CC}–π^*_{CO} interaction is deduced.[370] While the n–π_{CC} interaction is just of the type that is required in the Labhart–Wagnière model to explain the $n\pi^*$ enhancement, the π_{CC}–π^*_{CO} interaction appears very large, particularly since 7-norbornenone has only an 0.4-eV interaction of this type.
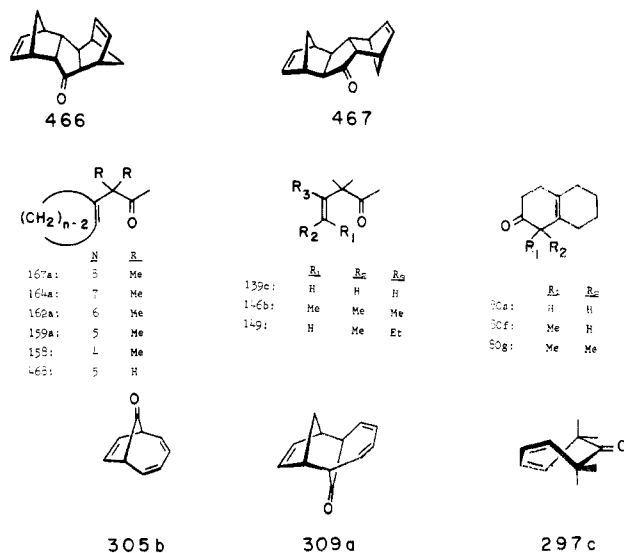
TABLE XXXVI. Photoelectron Spectra of
β,γ-Unsaturated Carbonyl Compounds

Compound	Vertical ionization potentials (eV)	Ref
β,γ-Unsaturated Ketones		
3-Cyclopentenone	9.44(n), 9.98(π)	369
7-Norbornenone	9.19(n), 9.62(π)	370
2-Norbornenone	8.90(n), 10.10(π)	370
167a	8.62(n), 9.40(π)	371
164a	8.68(n), 9.39(π)	371
162a	8.69(n), 9.45(π)	371
159a	8.73(n), 9.51(π)	371
158	8.84(n), 9.69(π)	371
468	8.71(n), 9.65(π)	371
139c	9.21(n), 10.26(π)	371
146b	8.48(n), 9.26(π)	371
149	8.67(n), 9.46(π)	371
80a	8.68(π), 9.23(n)	371
80fa	8.64(π), 9.16(n)	371
80g	8.55(π), 8.96(n)	371
$\beta,\gamma,\delta,\epsilon$-Unsaturated Ketones		
Bicyclo[4.2.1]nonatrien- 9-one (305b)	8.57(a''π), 9.57(n), 9.91(a'π), 11.14(a'π)	374
309a	8.51(a'',$\pi = \psi_2$), 9.30(a'',n), 9.30(a',π), 10.96(a',$\pi = \psi_1$)	375
297c	8.63(b,n), 9.10(a,$\pi = \psi_1$), 10.69(b,$\pi = \psi_1$)	375
α-Phenyl Aldehydes		
Phenylacetaldehyde	9.15(b$_1$-Ar,π) 9.56(a$_2$-Ar,π) 10.08(n)	376
Enol Esters		
Vinyl acetate	9.85(π), 10.73(n)	375
β-Diketones		
1,3-Cyclopentanedione	9.53(n$_-$), 10.40(n$_+$)	372
2-Methyl-1,3-cyclo- pentanedione	9.40(n$_-$), 10.18(n$_+$)	372
2-Ethyl-1,3-cyclo- pentanedione	9.35(n$_-$), 10.11(n$_+$)	372
2,2-Dimethyl-1,3- cyclopentanedione	9.34(n$_-$), 10.05(n$_+$)	372
1,3-Cyclohexanedione	9.60(n$_-$), 10.04(n$_+$)	372
2-Methyl-1,3-cyclo- hexanedione	9.48(n$_-$), 9.81(n$_+$)	372
5,5-Dimethyl-1,3-cyclo- hexanedione	9.46(n$_-$), 9.92(n$_+$)	372
2,5,5-Trimethyl-1,3- cyclohexanedione	9.30(n$_-$), 9.64(n$_+$)	372
2-Isopropyl-1,3-cyclo- hexanedione	9.29(n$_-$), 9.61(n$_+$)	372
2-tert-Butyl-1,3-cyclo- hexanedione	9.15(n$_-$), 9.62(n$_+$)	372
2,2,5,5-Tetramethyl- 1,3-cyclohexanedione	9.13(n$_-$), 9.52(n$_+$)	372

TABLE XXXVII. Minimum n–π_{CC} Interactions (PES)
and ϵ_{max}'s for Several β,γ-Unsaturated Ketones

Compound	$\Delta E(n\pi_{CC})_{min}$	ϵ_{max} (nπ^*)
3-Cyclopentenone	≡0	11 (300 nm)
7-Norbornenone	≡0	31 (274 nm)
2-Norbornenone	0.19	273 (306 nm)
80a	≡0	38 (281 nm)
162a	0.16	199 (299 nm)
139c	0.08	78 (290 nm)
305b	0.41	562 (320 nm)

In fact, we have proposed earlier in this review on the basis of semiempirical calculations that π_{CC}–π^*_{CO} interac-

466   467

167a: N=3 R=Me
164a: N=7 R=Me
162a: N=6 R=Me
159a: N=5 R=Me
158: N=4 R=Me
468: N=5 R=H

139e: R$_1$=H R$_2$=H R$_3$=H
146b: R$_1$=Me R$_2$=Me R$_3$=Me
149: R$_1$=H R$_2$=Me R$_3$=Et

80a: R$_1$=H R$_2$=H
80f: R$_1$=Me R$_2$=H
80g: R$_1$=Me R$_2$=Me

305b   309a   297c

tions are negligible. In our studies of an extensive series of β,γ-unsaturated carbonyls[371] and β-diketones,[372] a much larger inductive effect of the carbonyl group was proposed, and the π_{CC}–π^*_{CO} interaction was assumed to be negligible.[371] This conclusion has received recent support from MINDO/2 calculations by Dewar and coworkers.[373] Upon deletion of the resonance integrals involving through-space interactions, calculated π orbital energies did not change.[373]

The assignment of the lowest and next lowest ionizations to the π_{CC} and n orbitals, respectively, in the case of **80a** was unequivocal, owing to the presence of vibrational structure in the lowest ionization band. Since **80a** has little n–π_{CC} interaction due to the near-coplanarity of the carbonyl and alkene groups, the differences between the ionization potentials of **80a** and its isolated chromophores should result primarily from mutual inductive effects. In fact, the changes in n and π ionization potentials are similar to those of 3-cyclopentenone and 7-norbornenone, even though the extent of possible π_{CC}–π^*_{CO} interaction should be very different in these three compounds.[371] These compounds are prototypes of geometries in which no n–π_{CC} interaction occurs and in which no nπ^* enhancements are observed. In the remaining compounds studied (Table XXXVII), the differences between the observed changes in n ionization potentials and the estimated inductive changes expected for these ionization potentials were equated to the n–π_{CC} interaction. In all cases, the π orbital is stabilized to a larger extent than the sum of inductive and n–π_{CC} interaction would indicate. While it might be tempting to invoke π_{CC}–π^*_{CO} interactions, the blue shift which would result from such an interaction is not observed, and the following alternative explanation was proposed.[371] When a carbonyl and alkene group are incorporated into the same molecule in a "noninteracting geometry", for example (0,90), then indirect interactions, loosely termed "inductive", stabilize both orbitals. When a molecule in such a geometry (e.g., **80a**) is rotated into an "interacting geometry", then both orbitals are further stabilized by loss of hyperconjugative interactions with σ_{CH} and σ_{CC} orbitals. The n–π_{CC} is then "turned on" to raise the n orbital energy and further lower the π_{CC} orbital energy. Therefore, the n–π_{CC} interaction is larger than that calculated in the previously described way. Since the magnitude of the "loss of hyperconjugation" energy is unknown, the value of $\Delta E(n$–$\pi_{CC})_{min}$ listed in Table XXVII is a lower limit to the n–π interaction. $\Delta E(n\pi_{CC})_{min}$ is the difference between the observed change in ionization potential and the estimated inductive lowering of the n orbital energy caused by the alkene group. Table XXXVII also lists the ΔE (nπ_{CC})$_{min}$'s and the ϵ_{max}'s for several other compounds studied. There is a

trend toward higher ϵ_{max}'s for greater n–π_{CC} interaction, even though the ϵ_{max} depends on both n–π_{CC} interaction and π_{CC}–π^*_{CO} overlap.

The substituent effects on ionization potentials of **80a, 139c,** and **162a,** are as expected for electron-releasing groups, but the effect of α-alkylation of **80a** is of some interest. The first methyl (**80f**) causes 0.04 and 0.07 eV raising of the π and n orbital energies, respectively, while the second methyl (**80g**) causes further increases of 0.09 and 0.20 eV in these orbitals energies. Although by no means proven experimentally, the following hypothesis was proposed to account for this phenomenon: The first methyl substituent should assume a pseudoequatorial conformation in the half-chair and will lie approximately in the plane of the molecule, while the second methyl will be pseudoaxial and approximately perpendicular to the carbonyl and alkene planes. Calculations on suitable models indicate the latter disposition of the methyl will influence the n orbital energy more than the former. It is interesting that the expected effects on ORD and CD spectra will be in the same order as the effect on the n ionization potential.[371]

This type of analysis can be applied to other β,γ-unsaturated carbonyl systems. Bünzli, Frost, and Weiler have investigated the bridged 3,5-cycloheptadienone, **305b,**[374] and the analogs, **309a** and **297c,** have been studied in our laboratories.[375]

The n orbital ionization potential of **305b** (9.57 eV) is raised by 0.57 eV with respect to that estimated for a saturated analog. The increase of the π ionization potential of the 3-cyclopentenone moiety is 0.89 eV as compared to bicyclo-[4.2.1]nonatriene, while the ionization potentials of the symmetric (ψ_1) and antisymmetric (ψ_2) orbitals of the diene system are raised by 0.21 and 0.59 eV, respectively. Bünzli et al. have dissected the changes in ionization potentials into inductive n–π interactions. Their analysis leads to an estimate of 0.41 eV for the interaction of the n orbital and the diene highest occupied orbital (ψ_2).[374] Such a large interaction and the excellent overlap expected for π^*_{CO} and the diene lowest unoccupied molecule orbital (ψ_3) are compatible with the very large extinction coefficients for the nπ^* transition in **305b** (Table XXXVII).

In Bünzli et al.'s recent work, the earlier estimates of inductive effects in 3-cyclopentenone and 7-norbornenone are implicitly corrected. Thus, using an estimate of inductive effects which is the same whether or not π_{CC} and π^*_{CO} orbitals can interact, the lowering of the π orbital energies of both 3-cyclopentenone and 7-norbornenone caused by the inductive effect of the carbonyl is estimated as 0.88 eV, somewhat larger than the observed effect in these systems.

The inductive effect of a carbonyl group on the antisymmetric highest occupied diene orbital (ψ_2) of cyclopentadienone has recently been measured by Schweig and coworkers.[376] This system is particularly interesting, since the ψ_2–π^*_{CO} interaction is zero for symmetry reasons. The ψ_2 orbital energy is lowered by 0.7–0.8 eV by substitution of a carbonyl group into the appropriate cyclopentadiene to form a cyclopentadienone.[376]

Our studies of **309a** complement those of Bünzli et al. Although the ionization potentials of appropriate saturated analogs of **309a** are not known, the ionization potentials assigned as shown in Table XXXVI correlate well with the Bünzli et al. assignments. The smaller ψ_1–n split in **309a** than in **305b** is suggestive of smaller interaction in the former. This very qualitative deduction is compatible with the smaller ϵ_{max}(460 at 292 nm and 150 at 324 nm) observed for **309a** than for **305b** (562 at 320 nm).

The 3,5-cycloheptadienone **297c,** differs from the previous two examples in that **297c** is of C_2 symmetry, rather than of C_s symmetry. Thus, the n orbital (b) of **297c** can interact with

ψ_1 (b), but not with ψ_2 (a) of the diene. The assignments given in Table XXXVI are not completely certain, but are compatible with the following interpretation. The methyls in **297c** will raise all of the orbital energies as compared to the orbital energies in **305b** or **309a.** Furthermore, the twisting of the diene moiety will result in stabilization of ψ_2 and destabilization of ψ_1 due to poorer overlap of the alkene moieties. Thus, the 0.59-eV stabilization of ψ_2 in **297c** is a result of both loss of the destabilizing interaction with the n orbital and of diene twisting, partially counteracted by an inductive destabilization by the methyls. The large destabilization of the n orbital in **297c** results from three effects: (1) the loss of stabilization caused by ψ_2 in **309a,** (2) the destabilization caused by methyls in **297c,** and (3) the destabilization by interaction with ψ_1 of the diene in **297c.** The net destabilization of ψ_1 indicates that the methyl inductive and diene twisting destabilization effects override the stabilizing interaction with the n orbital. Although a direct evaluation of the ψ_1–n interaction is not possible, a relatively large value of 0.2–0.6 eV can be estimated. The strongly enhanced nπ^* absorption in **297c** probably is not produced by appreciable $\psi_1 \rightarrow \pi^*_{CO}$ charge transfer, and cannot, for symmetry reasons, arise by coupling of the nπ^*_{CO} and $\psi_2 \rightarrow \psi_3$ transitions. However, n $\rightarrow \psi_3$ charge transfer is likely, and these orbitals overlap quite effectively.[335]

A few other β,γ-unsaturated carbonyls have been investigated. The spectrum of phenylacetaldehyde reported by Rabalais and Colton reveals an unexpected feature; namely, both benzene HO and NHO orbital energies are lowered to about the same extent[377] from their estimated orbital energies in appropriate models. The assignments in the table are those of Rabalais and Colton.[377] Using these assignments, both the symmetric (b₁) and antisymmetric (a₂) orbitals (with respect to an assumed plane of symmetry—the C_{2v} designations are given in parentheses) of benzene are lowered to approximately the same extent. Since the b₁ orbital of benzene would interact more strongly with the aldehyde n orbital than the a₂ orbital, the approximately equal stabilization of these two benzene π orbitals must result from a relatively large inductive stabilization of the b₁ orbital, partially counteracted by the b₁–n interaction which raises the b₁–π orbital energy and lowers the n orbital energy.

We have studied the PE spectrum of vinyl acetate,[375] and the spectrum reveals little through-space interaction. Thus, the magnitudes of the π and n destabilization can be accounted for adequately assuming that only inductive effects operate.

A large series of cyclic β-diketones has also been studied in our laboratories.[372] The 1,3-cyclopentanediones must be nearly planar and cannot, therefore, have any n–π type interactions but may have appreciable through-bond interactions between the n orbitals of the carbonyls. As seen in Figure 16, this interaction must be appreciable, as a splitting of 0.87 eV is seen between the n_s and n_a orbitals. The inductive effect of a β-carbonyl group on the n orbital energy of another carbonyl is 0.71 eV. For cyclohexanediones, the inductive effect should be somewhat smaller. The observed lowering is 0.68 eV, very close to this estimate, indicating little nπ-type interaction. Since the inductive effect can account for the magnitude of the energy lowering, the small splitting (0.44 eV) in the n-orbital energies of 1,3-cyclohexanedione must be due to smaller through-bond mixing.

Some further insight into the magnitude of through-space vs. through-bond interactions may be gleaned from a PE study of γ,δ-unsaturated ketones reported by Brown, Hudec, and Mellor.[357] The endo,endo bis-γ,δ-unsaturated ketone **466** and its dihydro derivative do not exhibit enhanced nπ^* absorptions, nor do they have "σ-coupled" transitions at ~224 nm. The PE spectra of **466** and its dihydro, tetrahydro, and

deoxo analogs indicate that each π orbital lowers the energy of the n orbital by about 0.02 eV. The carbonyl causes an 0.26-eV lowering of a π_{CC} orbital energy.

The 0.02-eV n orbital change can be attributed to stabilization via through-bond σ inductive withdrawal by the π_{CC} orbital. In this and the preceding analysis, we have assumed that the "inductive effect" is not the same as orbital mixing, but results from modification of core potentials and/or a diminution of hyperconjugative interactions due to lowering of the requisite σ orbital energies. Thus, **466** will have no n-π_{CC} admixture, and, furthermore, the geometry is unfavorable for $\pi^*_{CC}-\pi^*_{CO}$ overlap, also required for enhancement.

The isomer **467** and its analogs exhibit quite different behavior. The n orbital energy of **466** is raised by about 0.08 eV by each γ,δ-double bond, while the energy of π_{CC} orbital is lowered 0.25 eV by carbonyl inclusion.

Assuming the inductive effects in **466** and **467** are the same and using the n orbital ionization potential to determine the extent of n-π_{CC} interaction, the n-π_{CC} interaction must amount to about 0.10 eV in **467**. The enhanced nπ^*_{CO} can be attributed to the n-π_{CC} interaction, and to the ideal geometry in **467** for through-bond $\pi^*_{CC}-\pi^*_{CO}$ overlap.

Finally, the spectrum of 4-azabicyclo[2.2.2]octan-2-one has been referred to by Hoffmann and coworkers.[325] The nitrogen and carbonyl lone pairs have ionization potentials of 8.24 and 9.03 eV. These orbitals are stabilized by 0.22 and 0.78 eV, respectively, with respect to those of isolated chromophore models. The geometry of this bicyclic system is ideal for coupling of the n orbitals, and Hoffmann and coworkers suggest that an interaction of about 0.23 eV is present in this system.[325]

IV. Primary Photochemical Processes in β,γ-Unsaturated Carbonyls

A. A Comparison with Isolated Chromophore Photochemistry

The second section of this review outlined the rich variety of photochemical processes which occur in β,γ-unsaturated carbonyls. In this section, the photochemistry of simpler ketones and alkenes will be compared to that of the bichromophoric systems reviewed here, and the various theories of photochemical reactivity in β,γ-unsaturated carbonyls will be reviewed. In this way, an attempt to identify the primary photochemical processes in β,γ-unsaturated carbonyls and the factors which influence the rates of these processes will be made.

1. Summary of β,γ-Unsaturated Carbonyl Photochemistry

In order to facilitate the aforementioned comparison, Table XXXVIII summarizes the photochemical reactions observed in β,γ-unsaturated carbonyls of various structural types. Table XXXVIII, in conjunction with Table XXXIII, summarizes the photochemical and spectroscopic data, respectively, for the β,γ-unsaturated carbonyls which have been studied.

In Table XXXVIII, the reactions observed on direct irradiation are listed in the following way: if a 1,3-shift has been observed for any examples of this type of compound, "reversible" or "irreversible" is entered, depending upon whether a photostationary state of the reactant and product is formed, or the product of the 1,3-shift does not revert to reactant upon photolysis. Under "Evidence for α-cleavage" are listed any photochemical reactions which occur upon direct irradiation that are indicative of α-cleavage, while "Other reactions" lists reactions such as alkene or carbonyl reduction which occur upon direct irradiation.

Under the heading, "Intersystem Crossing", a "Yes" indicates that direct and sensitized reactions give identical prod-

ucts, and quenching of direct irradiation products can be effected; a "No" indicates different products are formed upon direct or sensitized irradiation; a dash indicates that no sensitized reactions have been attempted or sensitized irradiation gives polymer, or unidentified products but intersystem crossing probably does not occur; and "Probable" indicates that reactions likely to be those of triplet states occur upon direct irradiation, but no definitive evidence is available as to the reactive excited state. The entries under "Sensitized irradiations" indicate triplet reactions which have been observed. "Not reported" indicates that either no sensitizations have been attempted, or that polymerization or uncharacterized products form upon sensitized irradiation.

2. Estimated Excited-State Energy Diagrams for β,γ-Unsaturated Carbonyls

To identify the primary photochemical processes in β,γ-unsaturated carbonyls and to understand the factors which influence these processes, identifications of the natures and energies of the various excited states of these species are required. Interactions between the carbonyl and alkene chromophores will influence the energies of the excited states and will make the nπ^* and $\pi\pi^*$ labels approximate, at best. Figures 17–19 give excited-state energies for representative classes of compounds based on isolated models. These state energies provide a basis for the following discussion of how interactions affect the various excited state energies and reactivities.

The choice of diagrams is based on the desire to gain insight into the following phenomena: (1) α-cleavage reactions in simple ketones are accelerated by α-substitution, while α-cleavage and/or 1,3-shifts are favored by α-substitution in β,γ-unsaturated carbonyls; (2) $\alpha,\beta,\beta',\gamma'$-unsaturated ketones and α-phenyl ketones intersystem cross efficiently as compared with other β,γ-unsaturated carbonyls; and (3) triplet reactions of β,γ-unsaturated ketones are generally much different from those of the singlets and, aside from 1,2-shifts, are characteristic of alkene π,π^* triplets.

The estimated excited-state energies shown in Figures 17–19 are taken for the most part from several reviews.[378–380] Original references can be found in those sources. For the bichromophoric molecules, the various excited states are those of suitable isolated chromophore models. The carbonyl excited-state energies are, for the most part, taken from Turro's recent review of organic photochemistry,[378] while detailed measurements and estimates of α,β-unsaturated ketone excited state energies can be found in recent luminescence studies of Cargill et al.[379] Some slight adjustments to lower energies are made in the figures for substituted compounds. For alkene triplet states, the numbers given are those of the perpendicular triplet, while the shaded area extends up to the energies for the 0–0 singlet–triplet transitions which presumably reflect the energies of the planar triplet species.[380]

After these estimates were made, Schexnayder and Engel studied the efficiency of energy transfer from several sensitizers to simple β,γ-unsaturated ketones. They concluded that the "vertical" $\pi\pi^*$ triplet has an energy of about 76 kcal/mol and is 2 to 4 kcal/mol below the nπ^* triplet state,[18a] in good accord with the estimates in the figures.

The singlet and triplet energies of simple alkenyl and aryl esters are known only approximately,[378] but the nπ^* singlet and triplet state energies of these species are considerably higher than those of ketones or aldehydes. Delocalization between the ester and alkene moieties is expected, so the estimates in Figure 19 are very approximate, at best. The excited-state energies of the aminoborane moiety are not well known, but assuming that the weak transitions which occur at

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TABLE XXXVIII. Summary of Photochemical Reactions of β,γ-Unsaturated Carbonyl Compounds

Type of compound	Direct irradiation			Intersystem crossing?	Sensitized irradiations	
	1,3-Shift	Evidence for α-cleavage	Other reactions		1,2-Shift	Other reactions
Bicyclo[3.2.0]hept-6-en-2-ones	Reversible		Alkene reduction; Alkene cycloadditions	No	Yes	
Bicyclo[4.2.0]hept-7-en-2-ones	Reversible	Ketene formation; Ketal formation; Decarbonylation	Alkene reduction		Not reported	
Bicyclo[3.2.0]hept-2-en-7-ones	No				Yes	1,3-shift
Bicyclo[2.2.1]hept-5-en-2-ones	Irreversible	Ketene formation; Ketal formation; Decarbonylation		No	Yes	
Bicyclo[4.2.0]oct-2-en-8-one	No	Ketene formation; Decarbonylation		No	Yes	
Bicyclo[2.2.2]octenone	Irreversible	Ketene formation		No	Yes	
Bicyclo[3.n.1]alk-2-en-(6 + n)-ones	Reversible	Decarbonylation			Not reported	
3-Cyclohexenones (α-Alkylated)	Irreversible			No	Yes	
3-Cyclohexenones (α-Unsubstituted)	No			Yes	Yes	
2-Vinylcyclobutanones	No	Decarbonylation; Epimerization		No	Yes	
3-Cycloalkenones (n = 7–10)	Reversible	Dienal formation; Decarbonylation; Epimerization	Type II cyclobutanol if β-Me		Not reported	
2-Vinylcycloalkanones	Reversible			Probable	Not reported	Cis,trans isomerization
3-Cyclododecenone	Reversible			Probable		Cis,trans isomerization; intramolecular [2 + 2] cycloaddition
3,8-Cyclodecadiene-1,6-dione	No					
3-Methylenecyclobutanones	Reversible	Decarbonylation	Oxetane with dienes	No	Not reported	
3-Methylenecyclohexanones	Reversible (stereospecific)	Aldehydes	ROH addition to alkene		Yes, if a cycloalkene	Cis,trans isomerization
Acyclic β,γ-unsaturated ketones	Reversible	Radical coupling products, decarbonylations	Type II cyclobutanol if β-methyl; intramolecular oxetane with electron rich alkene; cis,trans isomerization	No	Yes	Cis,trans isomerization; intramolecular [2 + 2] cycloaddition
Acetonylcycloalkenes	Irreversible	Radical coupling products	Type II cyclobutanol if β-alkyl; intramolecular oxetane	Yes, if not α,α-dialkyl	Yes	α-Cleavage; 1,3-shift; cis,trans isomerization if cycloalkene (n ≥ 7)
Acylcycloalkenes	Reversible	Radical coupling products		No	Yes	
3-Cyclopentenones	No	Decarbonylation		Yes, if not α,α-dialkyl	No	Decarbonylation
α,β,β',γ'-Unsaturated ketones	None, reversible and irreversible examples	Radical coupling products, ketene formation	Cyclobutanol if β-alkyl	Yes	Yes	Intramolecular [2 + 2] cycloaddition; cis,trans isomerization; α-cleavage: 1,3-shift; Di-π-methane
Bicyclo[3.n.2]alk(7 + n)-3,6-dien-2-ones		Ketene by intramolecular [3,3]		No		

Compound	Products/reactions	Reversible/occurrence	Concerted reaction	Concerted?	Radical pair or diradical?
2-Cyclobutenone	Electrocyclization; nπ* electrocyclization; Ketene	No			?
2,4-Cyclohexadienone and 2,4,6-cyclooctatrienone	ππ* 1,2-shift or cis,trans isomerization	No; Irreversible		Yes	?
δ-Keto-β,γ-unsaturated ketones	Intramolecular oxetane formation; Diene electrocyclization			Not reported	?
β,γ,δ,ε-Unsaturated ketones Cis,s-cis	Diene electrocyclization		Diene electrocyclization; intermolecular [2 + 2] addition	Not reported; No	Probable
Trans,s-cis / Trans,s-trans	1,5-Shifts	Reversible	1,3- and 1,5-shifts; cis,trans-isomerization	Yes	Yes; ?
3,5-Cycloheptadienones	Decarbonylation	Yes			Yes, if polycyclic or α,α,α',α'-tetrasubstd
β,γ-Unsaturated aldehydes	Decarbonylation; Reduction if derived radical not resonance stabilized	No	1,3-Shift	Yes (one example)	No, unless also, α,β-unsaturated
Enol esters	Decarbonylation; radical coupling; ketene loss.	Reversible	1,3-Shifts?		?
β-Diketones / α-Phenyl ketones	Decarbonylation	Reversible; No	1,3-Shifts? α-Cleavage and decarbonylation	Not reported; Not reported	Yes; Yes
α-Phenyl aldehydes / Aryl esters	Photoreduction; intramolecular oxetane; Decarbonylation; 1,5-Shifts; phenol formation	No; Yes		Not reported; Not reported	?; Probable

about 20 nm shorter wavelength than those of carbonyl compounds are $\sigma_{CB}\pi^*_{BN}$ transitions,[381-383] the singlet and triplet estimates in Figure 19 can be made. Figures 17–19 also list the estimated energies of the noninteracting radical pairs formed by α-cleavage. These values are taken from the recent extensive compilation of bond dissociation energies and radical heats of formation.[384] The bond dissociation energy of the aminoborane is considered to be essentially the same as that of the isoelectronic ketone, in the absence of experimental data for this value. The cleavages of C–B bonds in aminoboranes are observed upon photolysis at 300 nm,[319,320] so the diagram in Figure 19 is at least qualitatively correct.

3. Singlet Photochemistry

a. α-Cleavages and 1,3-Shifts

Are the 1,3-shifts of β,γ-unsaturated carbonyls concerted reactions, or do these reactions involve α-cleavage, formation of radical pairs or diradicals, and subsequent recombination? The reaction, if concerted, may be classified as a photochemically allowed $[_\pi2_s + _\sigma2_s]$ reaction or a $[1s,3s]$ sigmatropic shift.[385] Alternatively, the reaction could be concerted, but could be analyzed with the inclusion of the π_{CO} and n orbitals in the orbital array. Two stepwise mechanisms, one involving formation of a diradical, the other a radical pair, might also be envisioned. All of these are shown in Figure 20. Those labeled (b) and (c) are only slightly different, (c) indicating that the bonding changes shown in (b) produce an intermediate diradical rather than producing a continuous conversion to products.

The relevance of orbital symmetry considerations to excited state processes, particularly those involving nπ* excited states, has been discussed in many places.[385,386] At the very least, orbital symmetry analyses provide information about the shapes of ground- and excited-state potential surfaces. Michl has recently provided a general discussion of such surfaces which is relevant to the current discussion.[387,389] Since the sigmatropic shift is a $[1s,3s]$ ground-state orbital symmetry forbidden reaction, the ground-state surface will have an energy maximum at a geometry approximating the transition state for a $[1s,3s]$ shift, while the S_1 surface will have a minimum at the same geometry. Thus, an excited singlet β,γ-unsaturated carbonyl could fall into this minimum; internal conversion to the ground-state would be essentially instantaneous, and completion of the 1,3-shift bond changes or reversion to reactant would occur on this ground surface.[388] The lowest excited singlet should prefer a "tight biradicaloid" geometry of this kind rather than "loose biradicaloid" geometries such as implied by (b) or (c), according to the Michl analysis.

The differentiation between (b) and (c) is one of degree, much like Zimmerman's discussion of the concerted vs. stepwise mechanisms of the di-π-methane rearrangement. That is, the bonding changes could occur in a single continuous downhill process as represented by (b), or, alternatively, since the reaction is a ground-state forbidden one, a brief pause at the biradical geometry (c) might occur if this geometry represents a minimum in the excited-state potential surface. It is perhaps relevant that the interactions implied in (b) are those (n–π_{CC} and π_{CC}–π_{CO}) required for enhanced intensity of the nπ* transition.

Finally, (d) shows a radical pair intermediate which could be formed by α-cleavage without concomitant bonding of the acyl radical to the γ-carbon. The distinction between (a) and (d) is subtle, but formation of a true radical pair, (d), implies that reactions such as escape from the solvent cage, epimerization, and physical phenomena such as CIDNP in 1,3-shift products should be observable.

A number of experimental and theoretical investigations
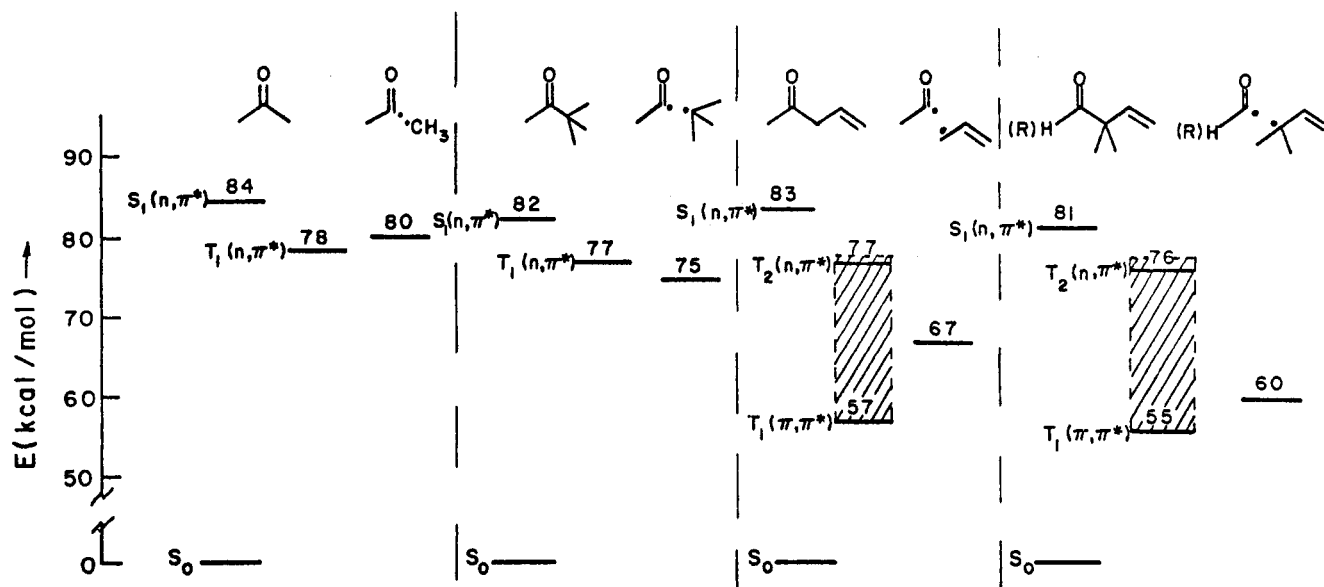
Figure 17. Approximate excited-state energies for simple ketones and β,γ-unsaturated ketones and their respective α-cleavage radical pairs.
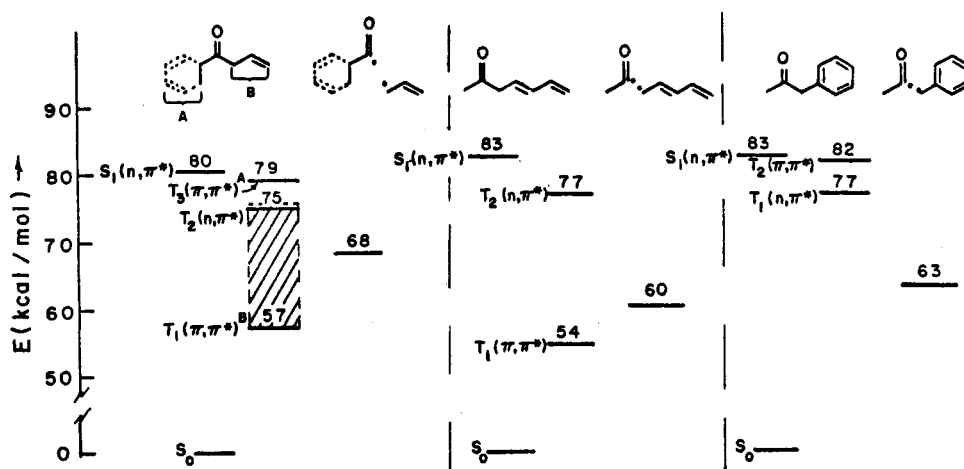
Figure 18. Approximate excited-state energies for β,γ-unsaturated aldehydes and ketones and α-cleavage radical pairs.
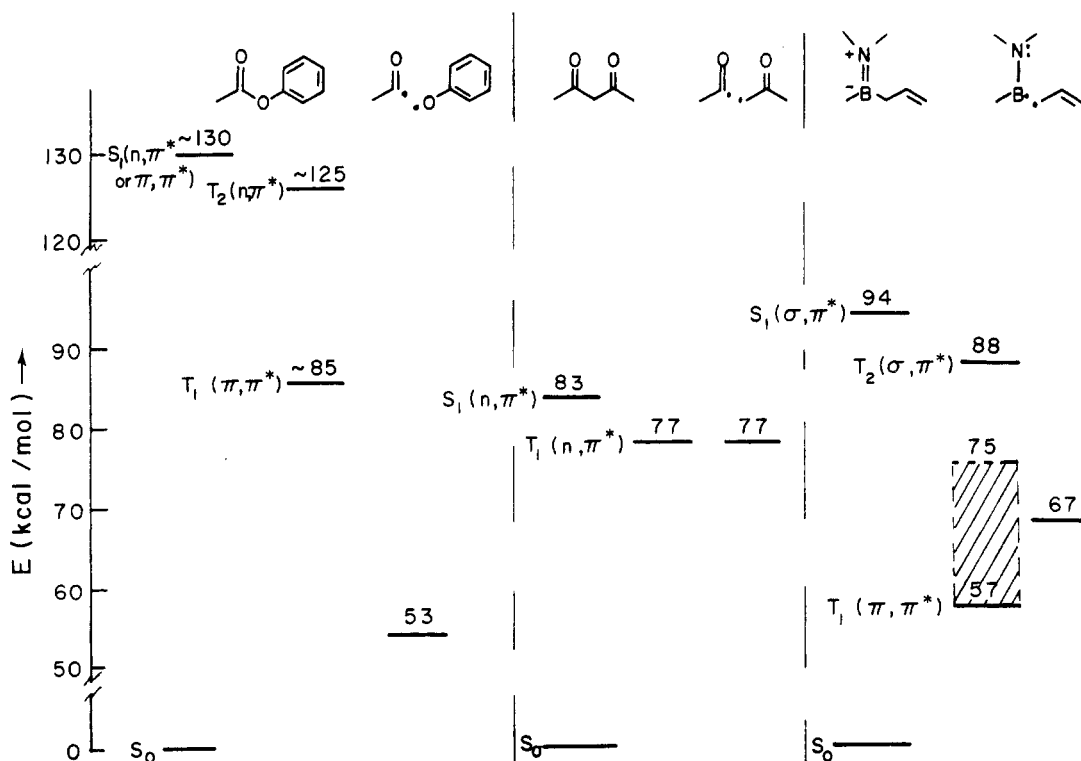
Figure 19. Approximate excited-state energies for β,γ-unsaturated carbonyl compounds and aminoboranes and α-cleavage radical pairs.
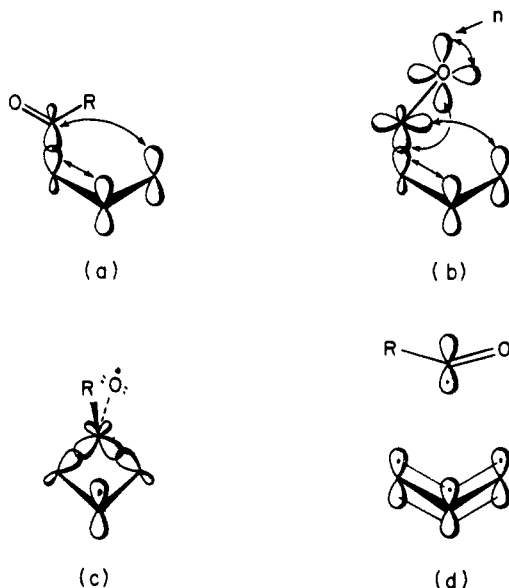
Figure 20. Possible mechanisms of the 1,3-shift of β,γ-unsaturated carbonyls: (a) concerted [1s,3s] sigmatropic shift $[_{\pi}2_s + {}_{\sigma}2_s]$; (b) concerted $[_{\pi}2_s + {}_{\sigma}2_s + {}_{\pi}2_s + {}_{\omega}2_a]$; (c) diradical intermediate via initial π_{CO}–π_{CC} bonding; (d) radical-pair intermediate.

into the proper description of "biradicals" have been published.[390-392] The description of biradicals and, presumably, radical pairs, as transition states, rather than as species occurring at energy minima, was proposed initially by Hoffmann et al., and has found support in a number of theoretical investigations. Although some biradicals and radical pairs recombine with an apparent activation energy, calculations indicate that trimethylene and tetramethylene biradicals are energetically located at broad, flat maxima on potential surfaces, rather than at energy minima. Presumably, a caged radical pair can exhibit similar behavior.

Berson and Salem have added a further complication to attempts to construct qualitatively correct potential surfaces.[393] These authors suggested that the transition states of orbital symmetry forbidden reactions will be stabilized with respect to radical pairs or biradicals involved in stepwise mechanisms owing to the interaction of "subjacent" orbitals, that is, orbitals lower than the highest occupied orbitals of the radical fragments.[393]

In order to incorporate all of these ideas into a potential energy surface in an even qualitative fashion, a multidimensional surface is required. It can qualitatively be described in the following manner. The excited singlet of a β,γ-unsaturated carbonyl will distort in the direction of a lengthened α-bond, which may, or may not, be accompanied by bonding to the γ carbon. If, because of the geometry of the excited ketone, or because of great stability of the radicals formed, the γ-bonding does not provide much stabilization, the excited singlet surface will meet the ground-state surface at a geometry described as a noninteracting radical pair. In a solvent, this caged radical pair can collapse rapidly to reactant or 1,3-shift product, or can diffuse out of the cage. If γ-bonding is favorable, the collapse of the excited singlet to a minimum in the surface is followed by rapid deactivation to the transition state of a concerted [1s,3s] sigmatropic shift, which can revert to reactants, form the [1s,3s] shift product stereospecifically, or can wander along the broad flat maximum in the ground-state surface toward a noninteracting radical pair geometry. Since the ground-state sigmatropic shift transition state, which is stabilized by subjacent orbital interactions, is only slightly more stable, at best, than a radical pair, then whether the reaction is best described as a concerted [1s,3s] sigmatropic

shift, or as an α-cleavage–recombination, can be changed by rather subtle substituent, solvent, and even irradiation wavelength variations.

Two recent articles suggest that the α-cleavage reaction is one in which the $n\pi^*$ singlet state correlates with the ground state of a radical pair when a plane of symmetry is preserved in the reaction. In cases of less symmetry, the excited-state surface "touches" (is very close in energy to) the ground-state surface in biradicaloid geometries.[393a]

The preceding discussion is a complex way of saying that the difference between a biradical mechanism and an α-cleavage–recombination mechanism is perhaps too subtle to be satisfactorily answered by experiment, and that a general solution to this problem is perhaps unattainable. However, a comparison of these abstract considerations to experiment does suggest that the previous model is capable of accounting for most of the experimental results.

As seen in Table XXXVII, most 1,3-shifts are accompanied by reactions such as decarbonylations, intramolecular disproportionations, and β-cleavages which are generally believed to involve diradicals or radical pairs with finite lifetimes. The compounds which appear to give 1,3-shifts unaccompanied by other reactions, such as the bicyclo[3.2.0]hept-6-en-2-ones and bicyclo[4.2.0]hept-7-en-2-ones, are ones in which two conditions are satisfied: (1) there are no clearly exothermic processes (such as loss of ketene) available from a hypothetical diradical, other than bond formation and (2) the system is sufficiently rigid so that the acyl and allyl radicals can never become sufficiently separated from one another to warrant the description "biradical". That is, the excited singlet will end up on the ground-state surface with the formal radical centers in close proximity, and only collapse to unrearranged, or to 1,3-shifted, products is anticipated.

The temperature effects and irreversibility observed in some 1,3-shifts can be explained qualitatively by this model. For example, the temperature effects noted by Scharf and Küsters[21] in the photochemistry of **35** can be explained by a qualitative diagram such as Figure 21. At low temperatures, excited singlets of either **35** or **36** can reach an S_1 surface minimum and internally convert to the ground-state surface (vertical arrow). From the point of initial deposition on the S_0 surface, there is essentially no barrier to formation of **38**. There is a very small barrier to attaining the "true biradical" geometry and finally the decarbonylation product, **39**, and a slightly larger barrier to collapse to **35**.

The irreversible 1,3-shifts may have surfaces such as that shown in Figure 21(a), except that the transition state for the [1s,3s] shift is shifted even more toward the photoreactive member of the 1,3-shift pair and away from the S_1 minimum. For example, 2-norbornenones, bicyclo[2.2.2]octenones, and the 3,5-fused-3-cyclohexenones all undergo irreversible 1,3-shifts to 2-vinylcyclobutanone systems, and irradiation of 2-vinylcyclobutanones gives decarbonylation or loss of ketene, but no 1,3-shift. In the bicyclooctenone case, this has been construed as evidence for the concerted nature of the 1,3-shift.[29] The description in Figure 21 is slightly different, in that it implies that there is no clear distinction between the concerted and biradical intermediate mechanisms, and that the precise nature of the bonding changes depends on both the exact shape of the potential surfaces and on the dynamics of movement along the S_1 and S_0 surfaces and of internal conversion between these surfaces. All of these can be influenced by subtle changes in structure of the β,γ-unsaturated carbonyl compound.

Quinkert, Stohrer, and their coworkers have recently proposed an alternative explanation for the unusual photochemical behavior of cyclobutanones.[394] They suggest that whereas most cyclic ketones readily α-cleave from n,π^* states, n,π^* excited states of cyclobutanones correlate with excited
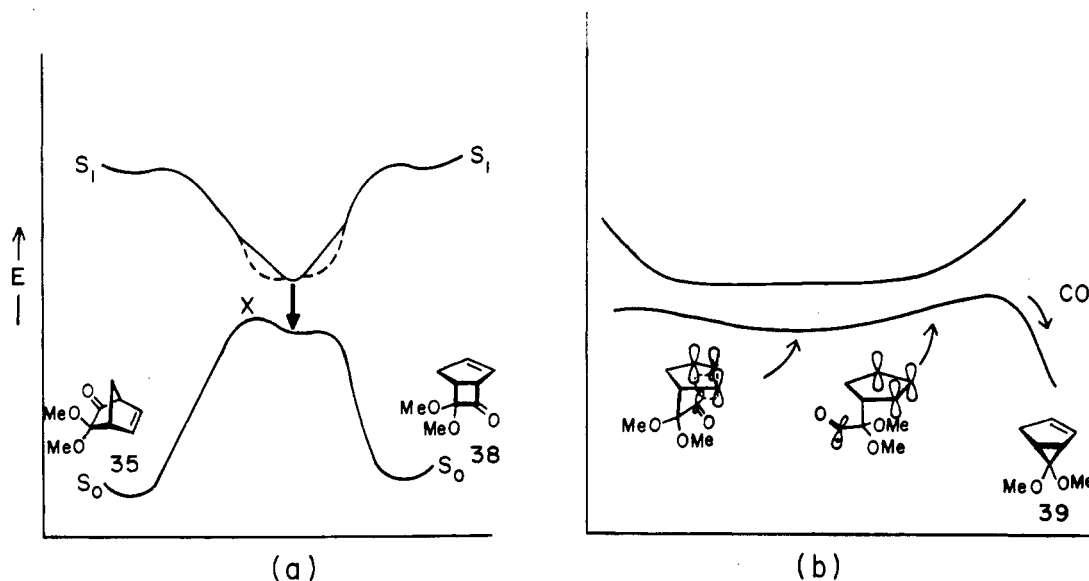
Figure 21. Hypothetical singlet potential surfaces for photochemistry of 3,3-dimethoxy-5-norbornenone: (a) reaction coordinate vs. progress of concerted [1s,3s] sigmatropic shift; (b) reaction coordinate cross section at S_1 minimum.

states of oxacarbene, from which an interstate process occurs, forming ground-state carbenes that can be trapped. In the absence of a trap for the carbene, it may open up to form an acyl–alkyl diradical.[394] The failure of cyclobutanones to give 1,3-shifts may arise from the exclusive formation of oxacarbenes, which then are either trapped by alcohols or lose ketene or CO.

One criterion for the concertedness of photochemical reactions, proposed by Kaupp and Prinzbach,[395] should be relevant to the 1,3-shift mechanism. A photoreversible reaction involving a diradical intermediate which partitions to the two members of the "equilibrium" without significant competing side reactions should have the sum of the quantum yields for forward and reverse reactions equal to 1. A number of [$_\pi$2 + $_\pi$2] reactions of this type have been observed.[395] Concerted reactions could have a quantum yield sum of greater than 1 according to the Kaupp analysis. Alternatively, Figure 21 is also compatible with the Kaupp "biradical intermediate", if S_1 is thermally equilibrated before intersystem crossing (unlikely, according to Michl[387,388]) or if the S_0 surface is sufficiently broad or has a shallow minimum. The 1,3-shifts of β,γ-unsaturated carbonyls for which quantum yields have been measured all have $\Phi_f + \Phi_r$ of less than unity.[455] Values of $\Phi_f + \Phi_r$ of 0.31,[74] 0.4,[85] and 0.5[90] have been measured for 1,3-acyl shifts. This indicates that the dotted lines in Figure 21(a) may more accurately represent the S_1 surface, since a common point on the S_0 hypersurface would then not necessarily be reached starting from either extreme of the S_1 potential surface. If a common point were reached, then $\Phi_f + \Phi_r$ should equal one, unless other modes of singlet deactivation were important.

A comparison of the 1,3-shift with type I reactions of simple ketones shows more clearly the experimental relationship between these types of photochemical reactions. Simple acyclic ketones undergo the type I reaction inefficiently, if at all, in solution.[396] Figure 17 shows the relative energies of acetone singlets and triplets and of a noninteracting radical pair. For simple ketones, the lowest singlet excited state could dissociate to the radical pair exothermically. However, the S_1 excited state should favor a "tight geometry",[388] and radiationless deactivation to ground-state acetone with one bond stretched will occur, from which vibrational deactivation to acetone is expected. The triplet state can dissociate only endothermically, even though triplets generally prefer loose geometries,[388] so that only vibrationally excited triplets should dissociate.

By contrast, tert-butyl ketones undergo α-cleavage reactions from both excited singlet and excited triplet states in solution.[396,397] As shown in Figure 17, the α-cleavage of both of these excited states is exothermic. Nevertheless, the idea that the S_1 radical pair should favor a tight geometry, and thus be deactivated to the S_0 surface at a geometry near the ketone minimum energy geometry, while the triplet should prefer a loose geometry which will lead to dissociation, is supported by the observation that the triplet α-cleavage is about 100 times faster than the singlet α-cleavage in aliphatic ketones.

Alicyclic ketones undergo the type I α-cleavage readily, but these reactions are typically triplet state reactions. Many studies of this process have been reported recently, and the weight of evidence indicates that α-substitution of the ketone accelerates the rate of the triplet α-cleavage, but slows down intersystem crossing. Turro and coworkers postulate a rather deep energy minimum for the $n\pi^*$ singlet excited state and a shallower minimum for the triplet state.[398]

Even in cyclic ketones, the rate of singlet α-cleavage and of intersystem crossing can be competitive if the biradical is sufficiently stabilized.[399] However, the inefficiency of the type I reaction in cyclic ketones is indicative of a tight geometry for the "biradical", and the constraints of the ring system will, in any case, prevent the biradical from straying very far from a geometry which can readily undergo cage recombination.

A recent study of cyclobutanones and methyl-substituted cyclobutanones reveals that α-methyls drastically decrease singlet lifetimes and intersystem crossing efficiencies while increasing α-cleavage rates.[400]

Turning to the β,γ-unsaturated ketones, Figure 17 indicates that the formation of a radical pair from either the singlet or triplet $n\pi^*$ state should be highly exothermic, and, as the previous discussion indicates, the tight [1s,3s] transition state geometry should be of even lower energy on the S_1 surface than the radical pair geometry. In order for the $n\pi^*$ singlet of a β,γ-unsaturated ketone to readily α-cleave or form the pericyclic [1s,3s] transition state geometry, the α-bond must be approximately parallel to the π orbital, so that allyl resonance can stabilize the biradical and/or the carbonyl orbital can overlap with the π system at the γ end. Although this geometrical requirement has not been unequivocally tested for β,γ-unsaturated ketones, the behavior of β,γ-unsaturated aldehyde 348, studied by Schaffner and coworkers,[232] exemplifies this geometrical requirement.

The model represented by Figure 21 seems to satisfactori-

ly account for singlet β,γ-unsaturated ketone photochemistry and implies that the lack of intersystem crossing observed in these systems is the result of accelerated α-cleavage ($>10^9$ sec^{-1}) in these systems which results from the stability of the acyl–allyl radical pair, whether or not this is accompanied by γ-bridging. Engel and coworkers have provided a test of this model in their study of the effect of α-substitution on competition between 1,3-shifts and intersystem crossing.[47] As recounted earlier, 80a intersystem crosses without detectable

	R	R'		R
a:	H	H	a:	H
f:	Me	H	d:	Me
g:	Me	Me		
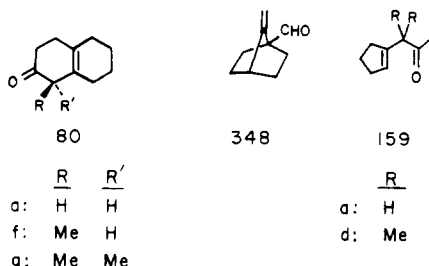
1,3-shift to give an oxa-di-π-methane product from the triplet state. This system is analogous to Schaffner's aldehyde, 348, in that the ground-state geometry, (and presumably that of the nπ^* excited singlet) does not allow allylic resonance to develop when the α bond stretches. In fact, this compound should resemble simple cyclic ketones which intersystem cross faster than they undergo α-cleavage. If α-cleavage occurs at all, the biradical is in a very "tight geometry" which will recombine on the ground-state surface. Upon α-methylation, singlet α-cleavage should become competitive with intersystem crossing even if no allylic resonance is attained as the α bond stretches. Experimentally, both the 1,3-shifts and intersystem crossing occur in 80f, while only the 1,3-shift occurs in 80g. Engel and coworkers estimate that the ratio of singlet α-cleavage to intersystem crossing increases 150 times on going from 80a to 80g, and the work of Turro et al.[398] indicates that the intersystem crossing rate should be halved by α-dimethylation. Thus, most of the change is due to accelerated α-cleavage.[47] This example seems to be one in which α-cleavage must precede any carbonyl bonding to the γ carbon.

Another interesting example of the effect of α-methylation was reported by Engel and Schexnayder.[95,101] Whereas 159a undergoes α-cleavage (a trace of biacetyl is formed) and a 1,3-shift, 159d gives both the 1,3 shift product and a triplet oxa-di-π-methane product.

The photochemistry of other β,γ-unsaturated carbonyls can be understood by means of the hypothesis that the [1s,3s] transition-state geometry and the separated radical pair geometry are nearly equienergetic on both the excited singlet and ground-state surfaces. Schaffner's explanation of β,γ-unsaturated aldehyde photochemistry anticipated this approach. That is, the interacting radical pair 339, proposed by Schaffner, is that species called here the [1s,3s] transition state. It will be connected to a caged radical pair by a rather flat potential surface. The question of concert in the decarbonylation is again subject to some equivocation. That is, for that fraction of the excited singlet which is deposited on the ground-state surface in the [1s,3s] transition state geometry, rotation to a geometry favorable for hydrogen transfer should be facile, but some dissociation to a caged radical pair, and occasional escape from the cage can occur. Wavelength effects and different amounts of deuterium incorporation can be rationalized by hypothesizing that different rotamers will be "funneled" onto the ground-state surface at different geometries, some less suitable for hydrogen transfer than others. In the less favorable geometries, dissociation can then compete with rotation to a geometry in which hydrogen abstraction occurs.

The decarbonylation of 3-cyclopentenones is a particularly interesting phenomenon which is apparently complicated by the fact that α-substitution is required for efficient decarbonylation, but there is some stereospecificity in the decarbonylation. For this decarbonylation, there are four possible pericyclic geometries: linear–disrotatory, nonlinear–conrotatory, linear–conrotatory, and nonlinear–disrotatory, where the specifications are for the sense of extrusion of CO and for rotation of the α carbons, respectively.[385] The last two are thermally forbidden, so there should be maxima on their ground state, and minima on their lowest excited singlet surfaces. However, decarbonylations appear to involve mainly triplet states. The inefficiency of singlet decarbonylation relative to intersystem crossing is of interest, since geometrically feasible minima (especially the linear–conrotatory) on the singlet surface should be reached easily. Perhaps this pericyclic transition state geometry is too "tight" to dissociate readily, although accelerated intersystem crossing would be a more attractive explanation (see the discussion of triplet α-cleavage).

Engel and Schexnayder reported that α-cleavage and decarbonylation occurred upon irradiation of bis(α,α-dimethylallyl) ketone in solution at room temperature, but that only a 1,3-shift occurred upon irradiation in a glass at 77°K.[102] This is compatible with a rather flat potential surface separating the [1s,3s] transition state and a separated radical pair. The lower temperature and large cage effect of the glassy medium confines the pathway of deactivation of the spectroscopic singlet to a geometry passing through or near the [1s,3s] transition-state geometry.

The singlet 1,3- and 1,5-shifts in $\beta,\gamma,\delta,\epsilon$-unsaturated ketones could involve the quasi-concerted type of mechanism proposed here for 1,3-shifts. It is also likely that a ground-state [1s,3s] transition state geometry could (i) collapse to reactant or 1,3-shift product, (ii) isomerize without a substantial barrier to form an isomeric [1s,3s] geometry which could collapse to the 1,3- or 1,5-shift product, or (iii) dissociate to form a radical pair. All of these processes can probably occur on a relatively flat ground-state potential hypersurface. A similar model can account for the 1,3- and 1,5-shifts in the photo-Fries reactions of aryl esters. That is, the "tight" [1s,3s] geometry should be favored, but relatively easy access to a caged radical pair, with concomitant escape of some radicals, should be available.

It is interesting to note here the systems which do not undergo singlet 1,3-shifts or detectable singlet α-cleavage. The $\alpha,\beta,\beta',\gamma'$-unsaturated ketones, γ-keto-β,γ-unsaturated ketones, and α-aryl ketones all have $\pi\pi^*$ triplet states nearly degenerate with the singlet nπ^* states. Although the singlet α-cleavage in these compounds should be just as facile as that in the simpler compounds discussed here, intersystem crossing is accelerated and is much faster than α-cleavage from the singlet state (vide infra).

In a few cases, notably the 2-norbornenones and bicyclo-[3.2.0]hept-2-en-7-ones, the oxacarbene is formed in addition to 1,3-shift products. These systems are of course analogous to the saturated 2-norbornanones and cyclobutanones, where this phenomenon is also observed.[401] Morton and Turro have recently suggested that a noninteracting biradical is not formed in this reaction, but instead, an interacting (tight geometry) biradical is formed from the nπ^* singlet in which there is interaction between both carbonyl carbon and oxygen orbitals with the alkyl radical orbital.[401] This is essentially equivalent to a thermally forbidden [1s,2s] sigmatropic shift transition state with four electrons involved, and, as such, should be a minimum, or funnel, on the lowest excited singlet surface. When deposited on the ground-state surface in this geometry, recombination to reactant, collapse to oxacarbene, or dissociation to a free radical pair and hence to ketene and an alkene can occur. This geometry is another read-

ily accessible one on the ground-state surface discussed earlier.

In summary, the α-cleavages and 1,3-shifts of β,γ-unsaturated ketones appear to parallel phenomenologically the α-cleavages in saturated ketones. The β,γ-unsaturated ketones α-cleave much faster than they undergo intersystem crossing since a relatively stable acyl–allyl radical pair, further stabilized by 1,3 bridging represents a deep minimum (or funnel) on the singlet excited surface which can be reached with essentially no barrier from the nπ^* singlet excited state.

b. Oxetane Formation

All of the reactions discussed in the previous section involve α-cleavage to the ground-state [1s,3s] transition state and/or to radical pairs. However, several β,γ-unsaturated ketones which have a low π_{CC} ionization potential undergo intramolecular oxetane formation rather than α-cleavage reactions. Engel and Schexnayder have proposed that this occurs when a charge transfer ($\pi_{CC} \to \pi^*_{CO}$) configuration contributes substantially to the singlet excited state.[102] These authors also suggested that the decreases in the efficiencies of α-cleavages and 1,3-shifts as the ionization potential of the alkene moiety decreases can be attributed to increasing contributions of the $\pi_{CC} \to \pi^*_{CO}$ configurations to the singlet excited state.[102]

There is ample evidence in the literature to indicate that singlet or triplet exciplexes between excited states and good electron donors can form readily, and exciplex formation can be a mechanism for radiationless decay or cycloadduct formation. For example, Guttenplan and Cohen reported linear relationships between the ionization potentials of electron-donating quenchers such as amines, alkenes, and sulfides, and the log of the rate of quenching of benzophenone phosphorescence.[402]

In several β-phenyl ketones, the inefficiency of type II processes has been attributed to interaction of both nπ^* singlet[359] and triplet[403] excited states with the phenyl π orbitals. Intramolecular singlet exciplex formation has been invoked to account for the more rapid formation of the $\pi\pi^*$ triplet state of 5-hexenal from the nπ^* singlet than from the nπ^* triplet of this compound.[404]

Turro and coworkers have proposed that the nπ^* excited states of ketones are electrophilic in the plane of the carbonyl by virtue of the presence of a half-filled n orbital, but are nucleophilic above or below the plane of the carbonyl by virtue of the presence of the electron-rich π system.[396,405] This analysis is supported by a number of experimental studies,[405] as well as by Herndon's perturbation analysis of the Paterno–Büchi reaction.[406] Studies of acetone cycloadditions to conjugated dienes reveal that the nπ^* singlet adds to the diene at a rate proportional to that of acetone fluorescence quenching by the diene.[407] Formation of an exciplex between the ketone nπ^* singlet and the diene, followed by deactivation to ground state and/or collapse to oxetane, perhaps via a biradical intermediate, explains these results.

Sheehan proposed that oxetanes formed by attack of a carbonyl on a benzene ring are intermediates in the reactions of α-phenyl ketones substituted by electron-releasing groups on the aromatic ring.[291]

Thus, there is ample precedent for oxetane formation from electron-rich alkenes and ketone nπ^* singlets, but the crucial question concerns the competition between α-cleavage and oxetane formation. The Engel hypothesis[102] appears to account adequately for the increased rates of oxetane formation and of singlet deactivation as the ionization potential of the alkene decreases. A more detailed description is given later in the discussion of theories of cycloadditions. We expect, however, that the pathways to α-cleavage or to oxe-

tane formation are determined quite early after the absorption event. If the alkene is a sufficiently good electron-donor and a conformation such as shown below can be easily achieved
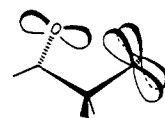
without substantial barriers, then intramolecular exciplex formation, leading to accelerated internal conversion to ground state and oxetane formation, can occur. Based on the results of Hansen and Lee,[404] intersystem crossing might be expected for such systems, also, although this has apparently not been observed in β,γ-unsaturated ketones.

c. Norrish Type II Reactions

The literature on Norrish type II reactions is voluminous, but several reviews have appeared.[378,396,408] The singlet Norrish type II reactions of β,γ-unsaturated ketones occur competitively with α-cleavage reactions if there is an abstractable γ-hydrogen (which necessitates the presence of a β-alkyl group) in the molecule, and if the molecule is sufficiently nonrigid for the hydrogen to be abstracted by the oxygen of the ketone. The systems for which the reaction has been observed (Table XXXVII) are either acyclic, or monocyclic with only one of the chromophores in the ring. The type II reactions of β,γ-unsaturated ketones give cyclobutanols and no cleavage products. This has been attributed to both the facts that an sp^2–sp^3 bond must be cleaved, and that the initially formed biradical will not be in a conformation favorable for cleavage of this sp^2–sp^3 single bond.[408] That is, in order for the cleavage to occur, a twisted alkyl radical **470**, would be required in order to satisfy the stereoelectronic requirements for cleavage of the intermediate biradical. The more favored conformation, **469**, which retains allylic resonance, can close to the cyclobutanol. There is ample experimental

469   470

evidence that both the strength of the CH bond[408] and the ground-state conformation of the ketone[409] determine the rate of hydrogen abstraction in type II processes, although in the case of singlet abstraction, reversion to ground state may simply provide a mechanism for singlet deactivation.[410]

4. Rates of Intersystem Crossing

The rates of intersystem crossing in aliphatic ketones, 10^8 sec^{-1}, are ordinarily sufficiently rapid compared with other singlet processes, that triplet reactions dominate the photochemistry of these species. However, as noted earlier, singlet α-cleavage competes favorably with intersystem crossing when a sufficiently stable radical pair is formed.[396,397] Similarly, singlet lifetimes are sufficiently great to enable type II reactions or bimolecular processes to occur. The β,γ-unsaturated ketones are species which can give very stable acyl–allyl radical pairs so that α-cleavage is faster than intersystem crossing for simple β,γ-unsaturated ketones.

There are, however, a number of β,γ-unsaturated carbonyls in which intersystem crossing has been facilitated to such an extent that these species no longer undergo singlet α-cleavage. The most straightforward examples to interpret are the $\alpha,\beta,\beta',\gamma'$-unsaturated carbonyls and the δ-keto-α,β-un-

saturated carbonyls. In α,β-unsaturated ketones, intersystem crossing is accelerated by spin–orbit coupling between the $^1n\pi^*$ and $^3\pi\pi^*$ states.[411] Although α,β-unsaturated ketones may have either a lowest $n\pi^*$ or $\pi\pi^*$ triplet state, the $\pi\pi^*$ triplet will be approximately equal in energy to the $n\pi^*$ singlet, and spin–orbit coupling will facilitate intersystem crossing.[411] Although it might appear at first glance that the β,γ-unsaturated ketones should also exhibit accelerated intersystem crossing due to interaction of the $n\pi^*$ singlet state with the $\pi\pi^*$ triplet state, the effect usually will be quite small due to the following conclusions of El-Sayed:[411] the coupling of $n\pi^*$ singlet and $\pi\pi^*$ triplet states under the influence of the spin–orbit operator occurs when the π^* orbital involved is the same for both states; in the case of α,β-unsaturated ketones, π^* is the same delocalized orbital in both the $n\pi^*$ and $\pi\pi^*$ states, whereas in β,γ-unsaturated ketones, there is at best a small amount of π^*_{CC} character in the $n\pi^*_{CO}$ state (either by π^*_{CC} overlap with π^*_{CO} or by $n\pi^*_{CO}$–$\pi_{CC}\pi^*_{CC}$ configuration interaction) and a small amount of π^*_{CO} character in the $\pi_{CC}\pi^*_{CC}$ state. Thus, as a first approximation, it can be estimated that intersystem crossing in nonconjugated β,γ-unsaturated ketones occurs with a rate constant of about 10^8 sec^{-1}, and that in conjugated $(\alpha,\beta,\beta',\gamma'$- or δ-keto-β,γ-) ketones with a rate constant of 10^{10}–10^{11} sec^{-1}. If α-cleavage occurs from the singlets of both of these species with a rate constant of about 5×10^9 sec^{-1}, then essentially only α-cleavage ($\geq 98\%$) will be observed from nonconjugated β,γ-unsaturated ketone singlets, and only intersystem crossing ($\geq 95\%$) will be observed from the conjugated compounds. These rate constants are also compatible with those typically observed for type II processes. Thus, singlet abstraction of a tertiary γ-hydrogen occurs at a rate of about 2×10^9 sec^{-1} in alkyl ketones,[396] and since abstraction of an allylic γ-hydrogen should be as fast or faster than abstraction of a tertiary γ-hydrogen, type II processes and α-cleavage should compete with each other and both be faster than intersystem crossing in nonconjugated β,γ-unsaturated ketones.

If these generalizations are accepted, then the species of special interest are those which deviate from these generalizations: that is, the nonconjugated species which do intersystem cross, and the conjugated ones that do not intersystem cross. Examples of these types (Table XXXVII) are treated in the following paragraphs.

The 3-cyclohexenones lacking α-substitution have been discussed earlier. These systems appear to intersystem cross at a normal rate, but the α-cleavage is retarded owing to the unfavorable conformation for assistance from allylic resonance. The medium-ring compounds, cyclodeca-3,8-diene-1,6-dione and 3-cyclododecenone, which undergo reactions expected of $\pi\pi^*$ triplets on direct irradiation, probably do not have enhanced intersystem crossing rates. Instead, the lack of α-substitution and the possibility of ground-state conformations unfavorable for allylic resonance as α-cleavage proceeds probably combine to disfavor α-cleavage relative to intersystem crossing. The monocyclic 3-cyclopentenones are further examples of this retardation of singlet α-cleavage. The near-planar ground-state geometry cannot α-cleave readily with ensuing allylic resonance, since the α bond lies near the alkene plane.

The α-phenyl ketones α-cleave via very short-lived triplet states. These species are unusual on two accounts: (1) intersystem crossing is faster than α-cleavage, and (2) the triplets undergo α-cleavage reactions. The last phenomenon is dealt with in the following section. The facility of intersystem crossing relative to α-cleavage is unusual, and, in fact there appear to be peculiar differences between α-phenyl ketones (e.g., dibenzyl ketone), α-phenylacetaldehydes (e.g., α-phenylisobutyraldehyde), and phenyl esters (e.g., phenyl acetate). For dibenzyl ketone, both Engel[269] and Robbins and East-

man[270] reported that α-cleavage occurred via a very short-lived triplet ($\tau < 10^{-10}$ sec) which could only be inefficiently quenched and could be sensitized only by acetone. The quantum yield of decarbonylation is high ($\Phi = 0.7$), and the weak fluorescence can be quenched by dienes.[269] The latter result indicates that the triplet state is shorter lived than the singlet, and the quantum yield indicates that efficient cage-recombination of α-cleavage products from the singlet state cannot account for the results. It also appears that intersystem crossing is not unusually fast, but that singlet α-cleavage is unusually slow.

The studies of Schaffner and coworkers led to the conclusion that an excited triplet was responsible for α-cleavage in α-phenyl aldehydes.[298–300] Although CIDNP characteristic of triplet radical pairs was observed in the decarbonylated products, the triplet state α-cleavage was considered to be of minor significance, since triplet sensitization and quenching failed. However, in the light of the dibenzyl ketone results, a very short-lived triplet state cannot be ruled out for these reactions. CIDNP studies, as well as the failures of sensitization and quenching, lead to the conclusion that the photo-Fries reaction of phenyl acetate involves cleavage of the $n\pi^*$ singlet state.[310,311] The last conclusion appears to be questionable, since the triplet states of acyl esters are probably too high for easy sensitization, while the triplet state could be unquenchable.

Assuming that all of the conclusions in the preceding paragraph are correct, the dibenzyl ketone result is anomalous. On the other hand, all of these species could be α-cleaving via a very short-lived triplet state. Although no compelling explanation can be suggested to explain the anomaly (or anomalies), it is possible that the singlets of α-phenyl carbonyl species readily form singlet exciplexes which have no tendency to α-cleave and the formations of which provide mechanisms for intersystem crossing.

It has been proposed that the α-cleavage of β-diketones occurs via $n\pi^*$ singlets or via $n\pi^*$ triplets. In the absence of detailed mechanistic studies to prove the case, it appears likely that $n\pi^*$ singlets can α-cleave on direct irradiation, perhaps in competition with intersystem crossing, while $n\pi^*$ triplets can also α-cleave upon triplet sensitization.

The 3,5-cycloheptadienones present interesting examples where substitution and geometry have a profound effect upon the relative facility of α-cleavage (decarbonylation) and intersystem crossing. On the basis of CNDO/S calculations, we proposed the following rationale of the experimental results:[217] the singlet state decarbonylation of 3,5-cycloheptadienone without intersystem crossing is normal β,γ-unsaturated ketone behavior. However 2,2,7,7-tetramethyl-3,5-cycloheptadienone intersystem crosses at a rate competitive with that of decarbonylation, and since the methyl substitutions should promote α-cleavage, the intersystem crossing rate must be accelerated. Normally, α-methylation decreases the intersystem crossing rate, but CNDO/S calculations indicate that in the tetramethyl compound, the $^1n\pi^*$ state and a triplet state which we have called "^{3}CT" are nearly isoenergetic. The latter has a considerable contribution from an n → ψ_3 (diene) configuration, and spin–orbit coupling should be relatively large in the compound.

The 2,7-bridged-3,5-cycloheptadienone, **309a**, studied in our laboratories exhibits behavior compatible with this explanation. In nonpolar solvents, singlet decarbonylation competes with intersystem crossing and the lowest triplet state is of diene $\pi\pi^*$ nature, as demonstrated by the typical diene triplet dimers formed on direct or sensitized irradiation of concentrated solutions. In polar solvents, intersystem crossing occurs, and the oxa-di-π-methane product is formed on direct or sensitized irradiation. We concluded that in polar solvents the diene $\pi\pi^*$ ($\psi_2 \rightarrow \psi_3$) state, which has an appreciable
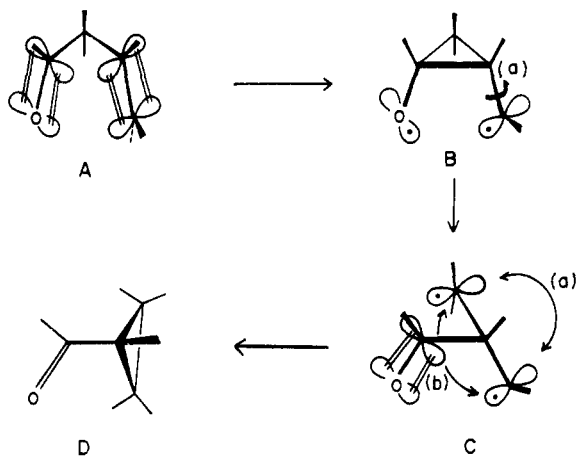
Figure 22. Possible radical intermediates in the oxa-di-π-methane rearrangement. Cyclization of C can give either (a) anti-disrotatory or (b) syn-disrotatory stereochemistries.

contribution from an n → ψ₃ charge-transfer configuration, is of nearly the same energy as the singlet nπ* state, and that intersystem crossing is facilitated by spin–orbit coupling.[217]

Although this explanation of the behavior of the 3,5-cyclo-heptadienone photochemistry is somewhat clouded by quantum mechanical detail, it does provide a consistent explanation for the behavior of these systems based on differences in rates of intersystem crossing, rather than on different rates of α-cleavage. The simpler bridged systems of this type, bicyclo[4.2.1]nonatrienone and bicyclo[4.2.1]nona-2,4-dien-9-one, behave more like simple β,γ-unsaturated ketones; that is, the singlet photochemistry (decarbonylations) and triplet photochemistry (oxa-di-π-methane rearrangements) are uncontaminated by intersystem crossing. We feel these compounds have accelerated decarbonylation, as compared to 309a, due to the greater strain in these species than in 309a.

5. Triplet Photochemistry

a. The Oxa-di-π-methane Rearrangement and Cis,Trans Isomerizations

There is little doubt that the excited state responsible for the oxa-di-π-methane rearrangement is best described as an alkene ππ* state. Figures 17–19 show that the triplet energies of alkenes are generally lower than those of ketones. Because of this, the relationship of this reaction to the triplet di-π-methane rearrangement observed in rigid 1,4-dienes is a close one. The possible diradical intermediates in the oxa-di-π-methane rearrangement are shown in Figure 22. Although an initial α-cleavage followed by recombination to form the diradical B has occasionally been proposed as a mechanism, this proposal is not viable since acyl–allyl radical pairs do not recombine in this fashion.[456] The diradicals represented by B and C in Figure 22 may either be discrete diradical minima of either triplet or singlet multiplicities, or, they may instead represent nonextrema on the potential energy hypersurface connecting A and D.[88] That is, the bonding changes depicted here may occur more or less simultaneously, as depicted by the Zimmerman analysis of the di-π-methane rearrangement given in Figure 11. Although the triplet state must reach a ground-state singlet minimum, spin–orbit coupling could be large in the reacting geometries facilitating crossings of singlet and triplet potential surfaces, and making a long pause at a triplet minimum before intersystem crossing unnecessary. Since the concerted reaction is thermally forbidden, there should be a maximum on the ground-state surface at some geometry between A and D, and a corresponding minimum, or funnel, on the singlet surface at this geometry.[387-389] However, the lowest excited singlet state shows no propensity to

reach this minimum. The reason for this is discussed in more detail later, but it qualitatively arises from contrasting geometrical distortions: α-bond stretching in the singlet nπ* state and C_{CO}–$C_β$ bridging in the triplet ππ* state.

Adopting the attitudes about potential surfaces relating diradicals and concerted reaction geometries used in the discussion of the 1,3-shift, the mechanism may involve essentially continuous bonding changes from excited triplet to product in some cases, but in others, intersystem crossing to the ground-state potential surface may occur at geometries near B or C, and, although no minima may be present on this surface at these geometries, flat maxima could result in kinetic and stereochemically behavior indistinguishable from that of a classical biradical.

As noted previously, if diradical intermediate B is formed in the oxa-di-π-methane rearrangement, rotation (a) is usually slower than reversion to A or conversion to C, since the reaction is often stereospecific. However, this bond is a good candidate for slow rotation, since the half-filled p orbital should overlap effectively with one of the occupied Walsh orbitals of cyclopropane, and the barrier to rotation could be substantial. In fact, even 1,4-biradicals lacking the cyclopropane may have substantial barriers to rotation.[392,412] Similarly, the disrotatory closure of biradical C is not necessarily a consequence of orbital symmetry constraints on bonding processes in excited C, but may be favored simply because of the more favorable overlap upon distortion in a disrotatory fashion toward closure. The experimental evidence on stereoselectivity in the oxa-di-π-methane rearrangement seems to require only that a specific geometry of A reacts, but biradical-type intermediates B and C can be formed. Conceptually, bonding changes represented by the A → B conversion should be downhill starting from the planar ππ* triplet of A, and intersystem crossing to the ground state surface at geometries represented by B, C, or a concerted geometry should be particularly facile. Michl has proposed essentially this idea, also.[388] He notes that the "loose" triplet biradicaloid geometries, B and C, should be minima on the triplet surface, and either B or C may essentially instantaneously be deposited on the ground-state surface, from which either A or D can be formed.[388]

Givens and coworkers suggested that the benzobicyclo[2.2.2]octenone 1,2-shift was concerted, since an alternative preparation of a species corresponding to C gave different product ratios.[29] This result is consistent with the attitudes adopted here, since C does not represent a long-lived intermediate, and formation of a species related to C from different precursors should give nonidentical species on the potential surface.

A number of workers have noted the "free-rotor" effect in di-π-methane and oxa-di-π-methane rearrangements. That is, the triplet states of β,γ-unsaturated ketones (or 1,4-dienes) in which the alkene moiety is unconstrained tend to undergo cis,trans isomerization faster than they undergo oxa-di-π-methane rearrangements. In this connection, it is interesting to estimate the relative energies of the various species in Figure 22. Using average bond energies[413] and strain considerations only, the relative energies of A, B, C, and D are 0, 101, 63, and 8 kcal/mol. The planar triplet of ethylene has an energy of 89 kcal/mol, while the perpendicular triplet has an energy of 57 kcal/mol.[380] Thus, if there were no particular stabilization afforded biradical B by overlap of radical centers with the cyclopropane bonds or with each other, the conversion of the planar triplet of A to B would be endothermic. The energy of B is probably overestimated by these simple considerations and, in any case, the "loose" triplet should be of lower energy than the "loose" singlet. However, B may well represent a maximum in the triplet surface unless the radical center on carbon is sufficiently stabilized. All of the experi-
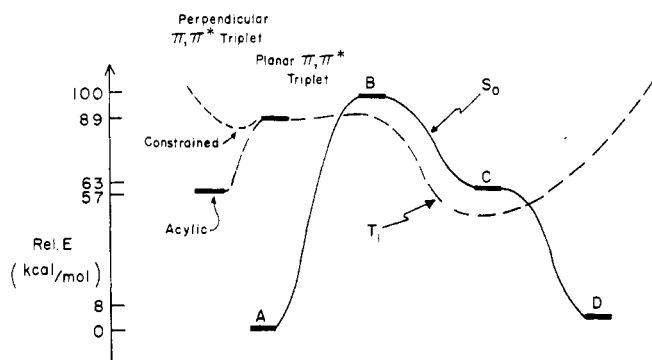
Figure 23. Hypothetical S_0 and T_1 surfaces along the oxa-di-π-methane reaction coordinate.

mental evidence amassed on the oxa-di-π-methane and di-π-methane rearrangements seems to be compatible with a triplet hypersurface in which B is a maximum slightly above the planar $\pi\pi^*$ triplet in energy. The situation hypothesized here is shown schematically in Figure 23. If the alkene is unconstrained, rotation to the perpendicular geometry occurs readily, and neither B nor C is energetically accessible from this low energy triplet. However, if rotation is prevented, the passage through geometry B should occur competitively with intersystem crossing to the ground-state surface and return to products. Any substituent which stabilizes B will facilitate the oxa-di-π-methane rearrangement. Since B is not an intermediate, no rotation about the formal single bond will occur in recovered product. At geometry C, facile intersystem crossing occurs, without pause unless this diradical has either highly stabilizing groups, or steric hindrance providing a barrier to closure to D.

The few examples of 1,2-shifts in systems capable of free-rotor deactivation of triplet states may represent examples where steric hindrance discourages rotation sufficiently, or where ground-state geometries are perfectly set up for bonding, so that passage over B occurs competitively.

One interesting lack of parallel between the oxa-di-π-methane and di-π-methane rearrangements is the failure of α-phenyl ketones, even those with lowest $\pi\pi^*$ triplet states to undergo the oxa-di-π-methane rearrangement, whereas the benzene nucleus readily enters into the di-π-methane rearrangement. This may arise from the very high energy of "transition state" B, which is further destabilized relative to A by the loss of aromatic resonance. In the case of a 3-phenylalkene, B may still be accessible owing to the lesser endothermicity of conversion of C=C to C—C than of C=O to C–O.

b. Triplet α-Cleavage

Although the generalization is commonly made that β,γ-unsaturated carbonyl singlets α-cleave (or 1,3-shift) and the triplets undergo the oxa-di-π-methane rearrangement, there are a number of well-documented examples of triplet α-cleavage. For the most part, the triplet α-cleavage occurs in those compounds for which the lowest triplet state is an $n\pi^*$ state. Thus dibenzyl ketone,[270,271] α-phenyl-1-indanone,[292] and benzoin[288] are compounds with lowest $n\pi^*$ triplets, and α-cleavage occurs rapidly from these $n\pi^*$ triplets. Figure 18 shows crudely the relationship of $n\pi^*$ and $\pi\pi^*$ triplets in these molecules. Bis(p-cyanobenzyl) ketone[270,271] and the biphenyl analog of 2-phenylindanone[292] are similar molecules with lowest π,π^* triplet states, and these triplets do not undergo α-cleavage reactions, even though the α-cleavage should be highly exothermic (Figure 18). These species might be expected to undergo oxa-di-π-methane rearrangements owing to the π,π^* nature of their lowest triplet states; however, this is not observed, and an attempted rationale of the
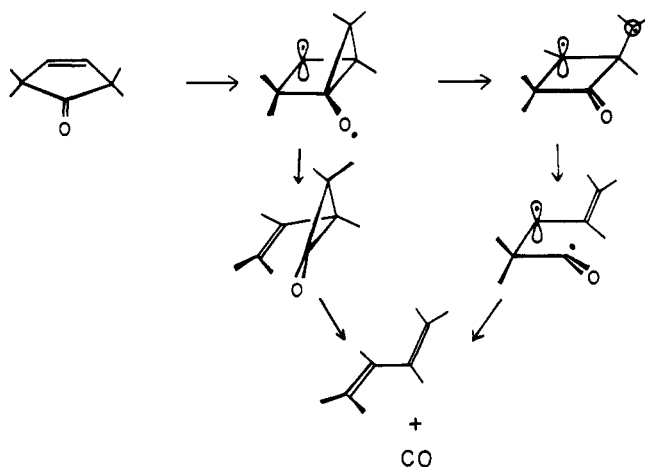

Figure 24. Hypothetical "foiled oxa-di-π-methane" mechanisms of triplet 3-cyclopentenone decarbonylation.

failure of such reactions is given in the preceding section. The benzoyl- and anisoylcyclopentenes, **204a** and **204b**, are species which should intersystem cross readily and undergo both α-cleavage and 1,3-shifts via their lowest $n\pi^*$ triplet states.

Schexnayder and Engel's results with 2-norbornenone seem to violate this generalization.[189] However, the $n\pi^*$ and $\pi\pi^*$ triplets may be very close in energy in this compound, so that reactions of both types are observed. This hypothesis is, of course, subject to experimental test.

One of the most intriguing results referred to earlier was Turro's report that certain 3-cyclopentenones undergo triplet decarbonylation with moderate stereospecificity.[123] The failure of the singlet states of **185** and **186** to undergo α-cleavage reactions followed by decarbonylation must be due to the unfavorable geometry for allylic stabilization of one radical center upon α-cleavage. The triplet α-cleavage (or concerted decarbonylation) is unusual, since the lowest triplet state is expected to be a $\pi\pi^*$ state, but oxa-di-π-methane rearrangements are not observed. The bicyclo[2.1.0]pentan-2-one products of hypothetical 1,2-shifts are unusually strained and may not be easily detectable, but it is conceivable that the decarbonylation might arise via a "foiled" oxa-di-π-methane mechanism. Several versions of this possibility are given in Figure 24. If such a mechanism occurs, stereospecificity can arise from both stereospecificity in bond-making processes, and in bond-breaking processes. As with other mechanisms discussed here, the diradical species shown in Figure 24 are not intended to be biradical minima. Turro's mechanism for this reaction, referred to earlier, is basically a concerted mechanism involving both linear and nonlinear extrusions of CO.[123]

Finally, the β-diketones are examples of compounds whose triplet states undergo α-cleavage reactions, but these species clearly have lowest $n\pi^*$ triplet states.

c. Cycloadditions

Several examples of intramolecular[12,13,68,69,102,131] and intermolecular[10,217] cycloadditions of β,γ-unsaturated ketones have been reported in previous sections. These reactions occur when the compound is sufficiently nonrigid so that some rotation about the double bond is possible, and when the molecule has a lowest $\pi\pi^*$ triplet state. These examples conform, therefore, to the usual mode of cycloadditions of simple alkenes.[378] The only exceptions to this generalization were reported by Cargill et al., who observed the cycloaddition of vinyl acetate to **4c** upon direct irradiation[10] and the intramolecular [2 + 2] cycloaddition of bis(β,γ-unsaturated) ketones to give homocubanones.[12,13]

B. Theoretical Treatments of β,γ-Unsaturated Carbonyl Photochemical Reactivity

In previous sections, several theoretical treatments of the spectra of β,γ-unsaturated carbonyls have been noted, and various suggestions made by a number of workers in the field to explain different aspects of the photochemical reactivity of these species have been recounted. In this concluding section, some theoretical calculations explicitly designed to explain β,γ-unsaturated carbonyl photochemistry will be reviewed, and the various theoretical suggestions made about photochemical reactivity will be summarized.

The Michl approach, which is an elegant synthesis of the ideas of a number of photochemists, has been used heavily in preceding sections.[387-389] In explicit applications to β,γ-unsaturated ketone photochemistry, Michl proposed that singlet states of these species prefer "tight" geometries, and the [1s,3s] transition state geometry is a funnel onto the ground-state surface.[388] The triplet 1,2-shifts arise from the preference for a "loose" geometry in which the distance between the parallel spins is maximized.[388]

However, in order to explain why some β,γ-unsaturated carbonyls undergo 1,2-shifts, and others undergo other reactions, the "loose" vs. "tight" generalizations do not suffice. We, and others, have attempted to look at initial bonding changes in excited states to explain why certain reactions are preferred. This procedure is not necessarily in conflict with that of Michl, but is complementary in that it provides a method to find which of several possible excited state minima or funnels can be reached most easily from a given vertical excited state.

When a molecule undergoes a vertical excitation, the resulting excited state will most likely be formed in a geometry different from the vibrationally relaxed geometry of that state. Certain antibonding interactions present in the ground state will be eliminated or weakened, while certain bonding interactions will develop or be strengthened. Qualitatively, geometrical changes from the vertical excited-state geometry may be dictated by these bond order changes.[414]

These ideas are used in their simplest forms in frontier molecular orbital treatments of excited state reactivity.[415] Thus a 1,3-shift is photochemically "allowed", as indicated by considerations of the interaction between a half-filled π orbital and an adjacent σ orbital.

Schuster, Underwood, and Knudsen presumed that both singlet and triplet reactions of β,γ-unsaturated ketones involved $n\pi^*$ excited states, and the spin polarizations for the singlet and triplet state would favor bonding of the carbonyl carbon to the γ carbon in the singlet state, and to the β carbon in the triplet state. That is, assuming an α spin for the half-occupied n orbital at oxygen in the excited state, and alternation of the net spin polarization through the α σ bond and the p orbitals of the alkene, then the β carbon will have net β spin density, and the γ net α spin density. For the triplet, in which the electron in the π^*_{CO} orbital will be of α spin, bonding to the β carbon (β spin) will be preferred, while the singlet state will have a π^*_{CO} orbital occupied by an electron of β spin, and bonding to the γ carbon (α spin) will be preferred.[3]

While this explanation does correctly rationalize the observed behavior, the $n\pi^*$ triplet states of β,γ-unsaturated carbonyls generally undergo α-cleavage reactions instead of 1,2-shifts. The treatment of the singlet-state rearrangement corresponds to the earlier discussion; that is, the excited singlet state probably has a minimum, or funnel, at a geometry in which both partial α-cleavage and some γ-bonding occur.

We proposed a different explanation based on differences in the nature of the excited singlet and excited triplet states.[335] CNDO/S calculations, as well as the several arguments given in the previous section indicate that the lowest singlet state is principally $n\pi^*$ (as expected), while the lowest triplet state is primarily a $\pi\pi^*$ state. The discussion in the previous section shows that the 1,2-shift, or oxa-di-methane rearrangement, is not characteristic of all triplet states of β,γ-unsaturated carbonyls, but only of those with lowest alkene-$\pi\pi^*$ triplet states. In fact, the differences in reactivity between singlets and triplets of β,γ-unsaturated carbonyls do not arise solely from the propensity of singlets to form "tight" minimum energy geometries and of the triplets to form "loose" minimum energy geometries. In fact, in those species with lowest $n\pi^*$ triplets, reactions identical with those of $n\pi^*$ singlets, such as α-cleavage reactions and even 1,3-shifts, are observed. The major difference between triplet and singlet $n\pi^*$ state reactions is one of rate, the former reacting faster in α-cleavage reactions.[397,398] Förster has proposed that inherent reactivity differences between singlets and triplets should not exist, "unless the S_1 and T_1 states have different orbital configurations".[416] This is precisely the situation encountered with β,γ-unsaturated carbonyls.

In our model,[335] as well as in simpler models,[417] the tendency of $n\pi^*$ states to α-cleave arises from the fact that n orbitals of carbonyl groups are significantly mixed with σ_α orbitals, and formation of the $n\pi^*$ state significantly weakens the α bond. The model also indicates that bonding between the carbonyl carbon and the γ carbon via the π systems of both moieties can occur, and, if this is geometrically feasible, such an interaction should lead to bonding and distortion toward the [1s,3s] shift geometry on the ground-state surface.[335]

The formation of oxetane in β,γ-unsaturated ketones containing an electron-rich alkene can also be rationalized by this approach. In a suitable geometry, $n\pi^*$ excitation should lead to bonding between the oxygen and the γ-carbon (see Figure 1 in ref 273). As electron-releasing groups are substituted on the double bond, the n orbital, which is mixed with the alkene π orbital via the σ_α bond, will take on more π character. Thus, the orbital "vacated" upon $n\pi^*$ excitation will have less α-bonding and more $O-C_\gamma$ antibonding as the ionization potential of the alkene moiety decreases. The $n\pi^*$ state will, therefore, have a greater tendency to form a bond between the oxygen and the γ carbon, and a lesser tendency to α-cleave as the alkene ionization potential decreases.

The delocalized ground-state model described in the preceding paragraph is an alternative to the configuration interaction, or excitation delocalization-type model proposed by Engel and Schexnayder.[101]

Finally, the MO model satisfactorily accounts for the triplet reactions of β,γ-unsaturated ketones. That is, if a lowest $n\pi^*$ state is populated, α-cleavage results from the weakened σ_α bond, while if the molecule has a lowest $\pi\pi^*$ triplet, rotation about the double bond may occur, or a bonding interaction between the π orbitals of the carbonyl carbon and C_β can ensue.[335] This results from the fact that the "π_{CC}" orbital (which is "vacated" in the "$\pi_{CC}\pi^*_{CC}$" state) is $C_{CO}-C_\beta$ bonding. As in di-π-methane systems, $\pi\pi^*$ excitation leads to a large increase in the $C_{CO}-C_\beta$ bond order, a large decrease in the $C_\beta-C_\delta$ bond order, and little change in the $C_\alpha-C_\beta$ bond order. These bond-order changes suggest precisely the bonding changes observed in $\pi\pi^*$ states of β,γ-unsaturated ketones.

V. Conclusion

The β,γ-unsaturated carbonyls exhibit a rich variety of photochemistry, and experimental studies are continually confirming some expectations and providing some surprises. A qualitative conceptual framework for the understanding of

these compounds has resulted from the fusion of experimental, spectroscopic, and theoretical studies of these compounds, and it is probable that understanding of these systems will soon attain a degree of profundity matching the profusion of experimental results observed for these systems.

VI. Appendix

Since the completion of this review in September 1974, a review of the photochemistry of β,γ-unsaturated ketones has appeared.[418] Although the review by Dauben, Lodder, and Ipaktschi covers only ketones, it is a useful adjunct to this review in that it is organized about reaction types, rather than structural types.[418]

The remaining additional references discussed below are indexed according to the section designations contained in the main text.

II.C. Scharf has reported that the complex rearrangements of 3,3-dimethoxy-2-norbornene (35) are mimicked for the most part by the 7-oxa derivative. However, decarbonylation of 7-oxa-35 is not observed, but, instead, fragmentation to dimethylketene and furan is observed.[419] These reactions and the 1,3-shift and oxacarbene formation are all believed to involve a common diradical formed from a singlet state of the reactant.

II.D. The photorearrangement of a novel compound of this type (65, R_3 = OMe, X–X = C_3H_4), corresponding formally to the Diels–Alder adduct of cycloheptatriene and dimethylketene, undergoes a singlet decarbonylation and allylic reclosure to form a bis-homobenzene derivative.[420]

II.F.2. Further studies of the octalone 80a have been reported by Engel, Ziffer, and their coworkers.[421] The 1,2-shift product is formed with the same efficiency upon acetone-sensitized irradiation as with direct irradiation (Φ = 0.05). However, ketone disappearance is rather high upon acetophenone or benzophenone irradiation, even though none of the 1,2-shift product is formed. The triplet energy of 80a is estimated as $\geq$74 kcal/mol, too high for triplet energy transfer from benzophenone or acetophenone, so it is suggested that an exciplex between excited ketone and 80a is formed, which can decay or give reaction products.[421] Oxetanes would seem to be logical candidates, although they have not been isolated.

II.F.3. Full papers have appeared concerning the photochemistry of 97–99,[422] and of 2-protoadamantenone.[423] Murray and coworkers have also reported that a homo-2-protoadamantenone undergoes mainly a 1,3-shift on direct irradiation, but prolonged irradiation of the 1,3-shift product (a bridged alkenylcyclopentanone) gives a 1,2-shift product.[424] Acetone-sensitized irradiation gives some 1,3-shift product, but direct absorption by the homoprotoadamantenone could be responsible for this observation.

II.G.3. The tetramethyl-3-methylenecyclohexanone 137a has been found to disappear upon acetophenone- or benzophenone-sensitized photolysis, but none of the 1,2-shift product is formed.[18a]

II.H.1. The acyclic compound 149 undergoes cis,trans isomerization upon acetone- (Φ = 0.20), acetophenone- (ϕ = 0.08), or benzophenone- (Φ = 0.01) sensitized photolysis.[18a] For the last compound, Φ for ketone disappearance is three times that of product formation, implying some type of sensitizer triplet reaction with the β,γ-unsaturated ketone.

A full paper discussing the photochemistry of acyclic β,γ-unsaturated ketones has appeared.[425] Some of the experimental results reported are covered in the main body of this review. A rich variety of sensitized cis,trans isomerizations and intramolecular [2 + 2] cycloadditions with bis(β,γ-unsaturated) ketones, and 1,3-shifts, α-cleavages, and cyclobutanol and oxetane formations upon direct irradiation are re-

ported. The direct irradiation of 3,3-dimethylpent-4-en-2-one was studied in the presence of a nitroxyl trap, and the results showed that at least 43% of the 1,3-shift observed for this compound occurs by recombination of free (noncaged) radicals. The remaining 57% of the 1,3-shift may arise by either a concerted mechanism or by radical-pair cage recombination. An interesting correlation between the quantum yield for ketone disappearance and our still unpublished ionization potentials of the alkene π orbitals is also given in this paper.[425] It is tentatively concluded that cage recombination limits the quantum yields for ketone disappearance (Φ_{-K}) for compounds with low alkene ionization potentials, and radiationless deactivation from an intramolecular CT complex further diminishes Φ_{-K} as the alkene IP is decreased.

II.H.2. A full paper on the systematic investigation of acetonylcycloalkenes has appeared.[426]

II.J.1.c.iv. Further work on the rearrangement of 232c has been reported.[427] Ketene intermediates formed from photolysis of the tropone–singlet oxygen adducts, 237m, have now been detected at $-196°$ by ir.[428] These rearrange at 25° to the stable products 244.

II.J.1.d.iv. Padwa and Vega have reported that an azobenzocyclooctatrienone undergoes both ring opening to ketene (or a 1,3-shift) and a 1,2-shift upon direct irradiation.[429]

II.J.3.b. Further intramolecular [2 + 2] cycloadditions of 2,4-cyclohexadienone dimers have been reported.[430] The natural product, asatone, which is a 2,6,6-trimethoxycyclohexadienone dimer, undergoes photochemical intramolecular [2 + 2] cycloaddition to the natural product isoasatone.[431]

II.K. Fuchs has reported the photochemistry of the simplest analog of 291.[432] The formal cyclopentadienone—maleimide adduct decarbonylates photochemically, and the resulting dienylamide undergoes electrocyclization, dehydrogenation, fragmentation, and a 1,2-shift. These products are said to arise from α-cleavage, and even the 1,2-shift product is said to arise by coupling of the resulting diradical.[432] The mechanism has been dismissed by most workers for 1,2-shifts in simpler systems.[456]

In a report overlooked by the reviewer, Jones reported in 1973 that a substituted analog of 294 undergoes reactions different from the parent. Thus, irradiation of the decarbonylated 3,4-diphenylcyclopentadienone dimer gives three products, all of which could be formed from a di-π-methane type biradical formed by primary 4–6 bonding.[433] However, there is still some doubt as to product structures, and, therefore, mechanisms of these reactions.

II.K.2. Schuster and coworkers have uncovered further complexities in the photochemistry of 2,2,7,7-tetramethylcycloheptadienone (297c).[434] Whereas irradiation of 297c at 300 nm gives both 1,2-shift (quenchable) and decarbonylation (unquenchable), irradiation into the S_2 maximum at 254 nm gives decarbonylation as well as cyclobutene (analogous to the parent cycloheptadienone *triplet* reaction) and 1,3-shift product. It is suggested that reactions from $S_1(n\pi^*)$, $S_2(\pi\pi^*)$, and $T_1(\pi\pi^*)$ are decarbonylation, electrocyclization and 1,3-shift, and 1,2-shift, respectively, and that similar wavelength dependence should be observable with other 3,5-cycloheptadienones.[434] A new calculational method, INDO/S, has been developed for unsaturated ketones.[434]

II.M. The discussion of vinylene carbonates overlooked the investigations reported by Stahlke, Heine, and Hartmann.[435] These authors reported that the aryl compounds 361 (R = aryl) undergo singlet decarbonylation reactions to give α-diketones.

II.O.1.a. Padwa and Hu have reported the facile photochemical decarbonylation of a phenylcyclopropanone.[436]

II.O.1.b. Weiss has reported the photochemistry of a three carbon bridged 2-indanone (400, $R_1–R_4$ = $CH_2CH(CO_2$-Me)CH_2). The four products formed could all arise from an ini-

tial quinodimethane formed by decarbonylation. Absence of sensitization by acetone and slight piperylene quenching implicated a singlet state in this reaction.[437]

II.O.1.c. Lewis and coworkers have reported further investigations of benzyl aryl ketone photochemistry.[438,439] Substitution effects on the rates of α-cleavage (see 405) led to the conclusion that the "transition state" for this reaction is appreciably polarized, the benzyl fragment bearing considerable positive charge, and the ketonic fragment appreciable negative charge, even though radical fragments are formed, ultimately.[438,439]

The parent benzobicyclo[3.2.1]octatrienone undergoes a di-π-methane rearrangement, analogous to that of the hexamethyl derivative 420. The quantum yields of this reaction (Φ(direct) = 0.02; Φ(sens) = 0.3) are an order of magnitude higher than those of analogs lacking the carbonyl group.[440]

II.O.3. The photochemistry of diphenylacetic anhydride has been studied.[441] As for the related esters and lactones, enhanced $n\pi^*$ absorptions are observed, and α-cleavage, with resulting decarboxylation, is facile when contrasted to the unreactivity of acetic anhydride.

Padwa and coworkers have found that 3,4-benzo-2-oxacyclopent-3-en-1-one and various derivatives undergo photochemical decarbonylation and subsequent rearrangements.[442]

II.Q. Further investigations of the di-π-methane "free rotor" effect have been reported.[443] Free rotation about a double bond is not, by itself, sufficient to prevent triplet di-π-methane rearrangement.

III.C.1.c. Additional photochemical and spectroscopic studies of "σ-coupled" systems (γ,δ-unsaturated ketones) have been reported.[444,445] Amrein and Schaffner have studied the spectroscopy of several bicyclic compounds containing both indanone and naphthalene chromophores.[446] The β-aryl ketones show enhanced $n\pi^*$ absorptions when the chromophores are well separated, but arranged in parallel planes. Emission from the naphthalene moiety is observed, and the intensity of emission is decreased in the compounds having the chromophores in close proximity.[446] An intramolecular exciplex interaction, essentially like that proposed by Engel to account for radiationless deactivation, is proposed. Other reports of β-amino[447] and α-, β-, γ-, and δ-halogen[448] effects on photoelectron and absorption spectra have been reported.

III.C.2. The failure of nonconjugated β,γ-unsaturated ketones to phosphoresce has now been documented.[18a]

IV.A.2. Hancock and coworkers and Fuss have studied emission and absorption spectroscopy of aminoboranes.[449,450] Both of these groups conclude that the intense long-wavelength absorption is due to a $\pi\pi^*$ transition, and Hancock and coworkers conclude that the fluorescent state is $\pi\pi^*$ in nature.[449] Hancock places the $\pi\pi^*$ singlet at 93–104 kcal/mol, and the $\sigma-\pi^*$ singlet state at around 95 kcal/mol,[449] similar to the position estimated in Figure 19.

IV.A.3.a. In their review of β,γ-unsaturated ketones, Dauben et al. state that there are three possible mechanisms for a 1,3-shift: (a) a dissociation–recombination mechanism, (b) a concerted 1,3-shift, and (c) a concerted [$_\pi 2 + _\sigma 2$] cycloaddition. They state that "Mechanisms (b) and (c) have not always been properly distinguished".[418] These mechanisms are not distinguished here because we see no difference, either experimentally determinable or theoretical between (b) and (c) except for the names. On the other hand, two other mechanisms not mentioned by Dauben et al. are shown in Figure 20 and discussed in the text.

Schuster and coworkers have measured fluorescence lifetimes for a number of β,γ-unsaturated ketones.[451] Dual emissions are observed (τ_1 = 0.5–5 nsec, τ_2 = 12–25 nsec). Assuming that the short-lived singlet state leads to 1,3-shifts

in β,γ-unsaturated ketones and to decarbonylation in tetramethylcycloheptadienone, rate constants of $\sim 10^8$ sec^{-1} were calculated for these processes. Contrary to the earlier conclusion, α-methylation of octalone 80a causes a small increase in singlet fluorescent lifetime.

Dalton has concluded that 1,3-shifts occur from T_2, rather than S_1, states.[452] Although this differs from the conclusion in the body of the review, it is compatible with the concept that α-cleavage and 1,3-shifts occur from $n\pi^*$ states (S_1 or T_2) regardless of multiplicity, while 1,2-shifts, cis,trans isomerizations, and the like are $\pi\pi^*$ reactions.

Other complications in the understanding of the apparently simple $n\pi^*$ α-cleavage reaction may arise from the fact that singlet photochemistry of aryl aldehydes and ketones has been shown recently to be wavelength dependent.[453] However, these results do show that the $n\pi^*$ nature of the excited state, rather than the multiplicity, causes α-cleavage to radical pairs.

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VII. References and Notes

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