Photochemistry of Bichromophoric Molecules. The Solution Phase Photoisomerization of 5-Hepten-2-one[1,2]

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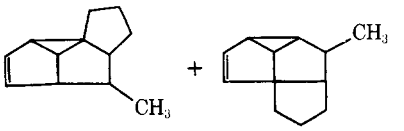
Abstract: Irradiation of *trans*-5-hepten-2-one (*trans*-I) with light of wavelength >280 nm in *n*-hexane at 20° gives as the two major products, 1,3-dimethyl-2-oxabicyclo[2.2.0]hexane (oxetane) (II) and *cis*-5-hepten-2-one (*cis*-I). Irradiation of *cis*-I gives *trans*-I but no isolable oxetane. The salient features of the mechanistic studies are (a) quantum efficiencies for *trans*-I to II and *cis*-I are 0.015 and 0.020, respectively; the quantum efficiency for conversion of *cis*-I to *trans*-I is 0.029, (b) neither oxetane formation nor isomerization is quenched by oxygen; piperylene quenches isomerization, but inefficiently and incompletely—it has a negligible effect on oxetane formation, (c) no intersystem crossing could be observed for *trans*-I by use of 0.038 *M cis*-piperylene, (d) photolysis of 4-methyl-5-hepten-2-one shows no sign of type II cleavage, even after 65% decomposition of the starting isomer, (e) no fluorescence is observable for *trans*-I. A mechanistic scheme, similar to that proposed for 6-phenyl-2-hexene, is outlined in which singlet exciplex formation is followed by radiationless decay and cycloaddition. Enhanced radiationless decay and singlet reactivity *via* such exciplexes appear to be a characteristic property of a number of bichromophoric molecules.

As part of a broad study of the photochemical and spectroscopic properties of nonconjugated bichromophoric molecules, we have recently reported on the 1-phenyl-2-butene,[3] 6-phenyl-2-hexene,[4] and 2-ethoxyethyl phenylacetate[5] molecules (*cf.* eq 1–3). The plethora of possible interactions for such systems is exemplified by the triplet energy transfer, singlet exciplex

$$\underset{\text{trans}}{C_6H_5CH_2CH{=}CHCH_3} \xrightleftharpoons[254\ nm]{h\nu} \underset{\text{cis}}{C_6H_5CH_2CH{=}CHCH_3} \quad (1)$$

$$\underset{\text{trans}}{C_6H_5CH_2CH_2CH_2CH{=}CHCH_3} \xrightarrow[254\ nm]{h\nu}$$

$$\underset{\text{cis}}{C_6H_5CH_2CH_2CH_2CH{=}CHCH_3} \; +$$

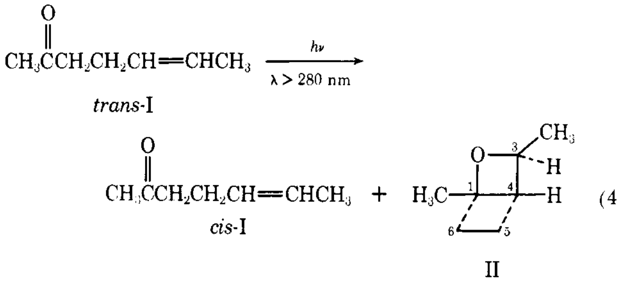


(2)

$$C_6H_5CH_2CO_2CH_2CH_2OCH_2CH_3 \xrightarrow[254\ nm]{h\nu}$$

$$C_6H_5CH_2CO_2H + CH_2{=}CHOCH_2CH_3 \quad (3)$$

and singlet energy transfer processes postulated for these three reactions, respectively. Some time ago, we chose the trans isomer of the title compound as a suitable model for studying internal keto-olefin interactions[6] and observed the reaction shown in eq 4.[7] In addition to its obvious interest as a further example of bichromophoric interaction, reaction 4 was particularly intriguing because the products involve ketone–olefin cycloaddition (*e.g.*, the Paterno–Buchi reaction) as well



$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CHCH_3 \xrightarrow[\lambda > 280\ nm]{h\nu}$$

trans-I

$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CHCH_3 \; + \quad (4)$$

cis-I

II

as ketone-sensitized trans–cis isomerization of an olefin. The *simultaneous* involvement of an *aliphatic* ketone in these two processes was, at the time of our report, a unique observation,[8] thus affording an unusual opportunity for exploring how the mechanisms of these intensely investigated reactions might be related.

Results

A. Preparation of *trans*- and *cis*-5-Hepten-2-one (*trans*-I and *cis*-I). *trans*-I was prepared by the addition of 1-chloro-2-butene to the anion of ethyl acetoacetate; basic hydrolysis, acidification, and distillation gave the enone in yields of *ca.* 50%. A mixture of the cis and trans isomers was isolated by preparative glpc on an SF-96 column and separated into 100% pure *trans*-I and *cis*-I using a AgBF$_4$–Carbowax 1540 column. The infrared spectrum of *trans*-I contains the carbonyl stretching band at 5.84 μ and the characteristic carbon–hydrogen out-of-plane bending band for a trans-disubstituted olefin at 10.33 μ. The nmr spectrum consists of a methyl doublet at δ 1.62, a methyl singlet at 2.03, and methylene and vinyl signals centered at 2.32 and 5.40, respectively. The uv spectrum has a λ_{max}

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[1] Organic Photochemistry. Part XVIII. Part XVII, R. Kleopfer and H. Morrison, *J. Amer. Chem. Soc.*, in press.

[2] Abstracted from the doctoral dissertation of Stephen R. Kurowsky, Purdue University, August 1970, Presented, in part, at the 157th National Meeting of the American Chemical Society, April 14–18, 1969, Minneapolis, Minn.

[3] H. Morrison and R. Peiffer, *J. Amer. Chem. Soc.*, **90**, 3428 (1968); H. Morrison, J. Pajak, and R. Peiffer, *ibid.*, **93**, 3978 (1971).

[4] (a) H. Morrison and W. I. Ferree, Jr., *Chem. Commun.*, 268 (1969); (b) W. Ferree, Jr., J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 5502 (1971).

[5] H. Morrison, R. Brainard, and D. Richardson, *Chem. Commun.*, 1653 (1968); R. Brainard and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 2685 (1971).

[6] H. Morrison, *Tetrahedron Lett.*, 3653 (1964).

[7] H. Morrison, *J. Amer. Chem. Soc.*, **87**, 932 (1965).

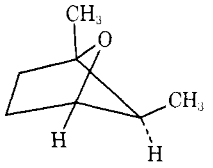
[8] Acetone had been shown to sensitize isomerization of fumaronitrile (J. Jenne, *Bull. Soc. Chim. Belg.*, **46**, 258 (1937)) and to form an adduct which has since been identified as the oxetane (J. J. Beereboom and M. S. von Wittenau, *J. Org. Chem.*, **30**, 1231 (1965)).

at 281 nm (ϵ 25); the mass spectrum shows a molecular ion at 112 m/e and a base peak at 43 m/e.

cis-I was prepared[9] by catalytic reduction of 5-heptyn-2-one, which in turn was made by condensation of ethyl acetoacetate and 1-chloro-2-butyne; the material was purified by glpc before use. Infrared absorption bands are observed at 5.84 and 14.38 μ; nmr bands are at δ 1.62, 2.04, 2.34, and 5.37.[9] The ultraviolet spectrum has a λ_{max} at 280 nm (ϵ 25); the mass spectrum shows a molecular ion at 112 m/e and a base peak at 43 m/e.

B. Photolysis of *trans*-I. A 0.24 M solution of *trans*-I in pentane was irradiated for 27 hr using a 450-W Hanovia lamp and a Corex glass filter ($\lambda > 260$ nm). Glpc analysis showed the presence of two major products and numerous minor components. The principal products were isolated by glpc and one was readily identified as *cis*-I by comparison with an authentic sample. The other product (II) was identified as the oxetane, 1,3-dimethyl-2-oxabicyclo[2.2.0]hexane, on the basis of the following data.

Elemental analysis confirmed II to be isomeric with the heptenone and the mass spectrum provided a molecular ion at 112 m/e. The infrared spectrum contained bands characteristic[10] of trimethylene oxides at 6.92, 8.04, and 10.14 μ with a band at 7.28 μ providing evidence for a CCH_3 group. The nmr spectrum provided confirmation of the oxetane structure as well as the stereochemistry at C3. It contains a doublet centered at δ 1.31 (CH_3C3), a singlet at 1.33 (CH_3C1), a complex multiplet centered at 2.33 (5 hydrogens), and a quartet of doublets centered at 4.56 (H-3; $J_{34} = 2$ Hz). These chemical shifts are compatible with those reported for 1-methyl-2-oxabicyclo[2.2.0]hexane[11] and 1,3,3-trimethyl-2-oxabicyclo[2.2.0]hexane;[12] the chemical shifts for the CH_3C3 and H3 moieties, as well as the splitting pattern for H3 are inconsistent with the isomeric cycloadduct, 1,6-dimethyl-2-oxabicyclo[2.2.1]hexane (III).[11-13]



III

The value of 2 Hz observed for J_{34} is consistent with a trans arrangement of these vicinal hydrogens, whence the dihedral angle is *ca.* 120°; the angle of 10° estimated for the cis configuration should result in a coupling constant of 8–9 Hz.[14] Further support for this stereochemical assignment is derived from the stereospecific formation of *trans*-I upon pyrolysis of II, either on a Carbowax 20 M glpc column at 165° or on a $AgBF_4$ column at 95°.[15,16]

Glpc analysis indicated that conversion to *cis*-I plateaus at about 22% of total substrate, whereas the oxetane content increases linearly with time. If the photolyses are restricted to conversions to *cis*-I of less than 10%, the oxetane:*cis*-I ratio is constant at 0.74 ± 0.08 (std dev).

C. Photolysis of *cis*-I. A 0.011 M solution of *cis*-I in *n*-pentane was irradiated under identical conditions to those described above and monitored by glpc. Initial formation of *trans*-I was noted followed by a gradual buildup of oxetane (II) and some of the minor components noted in the prolonged photolysis of *trans*-I. The oxetane was clearly a secondary product and no evidence could be found for the formation of an *isomeric* cycloadduct.

D. Quantum Efficiencies. These were determined at 280 ± 24 nm using a monochromator and a 200-W Hg–Xe compact arc. Samples were 0.018 M ketone in pentane and were not deoxygenated (see below); cis–trans conversions were limited to *ca.* 3% and starting material disappearance to *ca.* 7%.[17] The data are shown in Table I.[18]

Table I. Quantum Efficiences for *cis*- and *trans*-I[a]

Starting isomer	Oxetane (II)	ϕ olefin isomerization	Disappearance
trans-I	$0.015_5 \pm 0.000_5$	0.020 ± 0.002	0.065 ± 0.003
cis-I		$0.029_3 \pm 0.004$	0.054

[a] Pentane solvent, 20°, 0.018 M, errors represent standard deviations.

E. Quenching Experiments. Although several attempts were made to observe a degassing effect, no quenching by dissolved oxygen was detected, either for formation of the oxetane and *cis*-I, or for the disappearance of *trans*-I.

Quenching of trans → cis isomerization by *cis*-1,3-pentadiene was observed; the data are presented in Table II. Included in Table II are data for disappearance of *trans*-I and formation of oxetane (II) in the presence of quencher—the cycloaddition reaction is essentially insensitive to the presence of diene. The ϕ_0/ϕ values for *cis*-I formation and *trans*-I disappearance appear to level off at 4 M diene, with neat (10 M) diene still incapable of completely quenching the reaction.[19]

F. Triplet-Counting Experiments. Intersystem crossing efficiencies (ϕ_{isc}) were measured for *trans*-I and several substrate models using *cis*-1,3-pentadiene isomerization.[20] The data were corrected for back reac-

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[9] L. Crombie, S. H. Harper, R. E. Stedman, and D. Thompson, *J. Chem. Soc.*, 2445 (1951).

[10] G. M. Barrow and S. Searles, *J. Amer. Chem. Soc.*, **75**, 1175 (1953).

[11] R. Srinivasan, *ibid.*, **82**, 775 (1960).

[12] N. C. Yang, M. Nussim, and D. R. Coulson, *Tetrahedron Lett.*, 1525 (1965).

[13] Although we were unable to isolate any of compound III from the photolysis mixture, Yang has observed its formation by nmr, but in a 1:27 ratio to the oxetane, II (N. C. Yang, private communication).

[14] D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Inc., Englewood Cliffs, M. J., 1969, pp 185–186.

[15] 3,3-Dimethyl-2-oxabicyclo[2.2.0]hexane and 1,3,3-trimethyl-2-oxabicyclo[2.2.0]hexane have been shown to pyrolyze to 5-methyl-4-heptenal and 6-methyl-5-hepten-2-one, respectively; R. Srinivasan and K. A. Hill, *J. Amer. Chem. Soc.*, **88**, 3765 (1966).

[16] It is difficult to assess the significance of the *apparent* stereospecificity of both the photochemical 2 + 2 cycloaddition and the thermal fragmentation reaction, since the *cis*-oxetane analogous to II has not yet been isolated and studied. A complete study of the stereochemistry of oxetane fragmentation is in progress.

[17] Since conversions were minimized and a meaningful photostationary state unobtainable, no correction was made for back-reaction.

[18] An appreciable fraction of the disappearance of each isomer is unaccounted for and its source remains elusive; although several minor products are detectable by glpc, none is of individual significance.[13]

[19] Quenching of cis to trans isomerization of *cis*-I was not studied in detail, but one comparative experiment did give evidence that quenching of olefin isomerization for *cis*-I mirrors that observed for *trans*-I.

[20] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

Table II. Photolysis of *trans*-I in the Presence of *cis*-1,3-Pentadiene[a]

[Q], *M*	ϕ_0/ϕ		
	II	*cis*-I	*trans*-I disappearance
0.00	1.00	1.00	1.00
0.05	1.13	1.02	1.03
0.50	1.06	1.06	1.08
1.00	1.06	1.13	1.10
2.00	1.04	1.30	
3.00	1.07	1.31	1.22
4.00	1.05	1.43	
5.00	1.05	1.41	1.19
6.00	1.02	1.50	
7.00	1.01	1.44	1.35
8.00	1.00	1.49	
10.00	1.00	1.59	1.28

[a] Pentane solvent, 20°; 0.02 *M* heptenone, data are corrected for competitive light absorption by the pentadiene (λ = 313 nm).

tion[20] and for the amount of isomerization caused by acetone produced *in situ* (2-hexanone and 6-hepten-2-one). Solutions were adjusted so that the absorbances at 313 nm were identical (0.15). In order to facilitate comparison with data in the literature,[21] the ϕ_{isc} values are presented relative to acetone, with its value taken as 0.90.[21,22] As can be seen in Table III, no isomerization of *cis*-1,3-pentadiene is observed for either of the 5-hepten-2-ones under the conditions of these experiments.

Table III. Intersystem Crossing Efficiencies (ϕ_{isc})[a]

Ketone	ϕ_{isc}
Acetone	(0.90)
2-Hexanone	0.32[b]
6-Hepten-2-one	0.060
5-Heptyn-2-one	0.053
trans-5-Hepten-2-one (I)	0.00
trans-4-Methyl-5-hepten-2-one	0.00

[a] Measured in pentane solutions by isomerization of 4 × 10^{-2} *M* *cis*-1,3-pentadiene; irradiation at 313 nm and a value of 0.90 assumed for acetone.[21] [b] This value may be compared with a recently reported value of 0.27.[21]

G. Irradiation of *trans*-I at Low Temperature. The photoisomerization of *trans*-I to oxetane and *cis*-I was investigated in *n*-pentane at −23 ± 1°, and the oxetane:*cis*-I ratio was found to be 0.413 when the conversion to *cis*-I was 7.4%. The deviation from the room temperature ratio of 0.74 is reflected in a diminution in the oxetane formation and not in *cis*-I since the calculated and experimental values for conversion to *cis*-I agreed very well (the time required to achieve approximately 8.0% conversion was calculated from an actinometer solution run prior to the above experiment).

In order to determine whether the change in the oxetane:*cis*-I ratio is caused by the increased viscosity (η *ca.* 4 cP)[25] of the solvent at the lower temperature, a photolysis was also carried out at 17 ± 1° in normal tetradecane (η = 2.3 cP).[26] At a conversion to *cis*-I of 5.9%, the oxetane:*cis*-I ratio was 0.607.

H. Photosensitized Isomerization of *trans*-I. Benzophenone and acetophenone were used to study the effect of photosensitization on *trans*-I; trans → cis isomerization, but *not* oxetane formation, occurred under these conditions.

I. Photolysis of *trans*-4-Methyl-5-hepten-2-one. In order to determine how γ,δ-unsaturation affects other ketone photoproperties, this 4-methyl homolog was photolyzed in pentane at 20°. Although the irradiation was taken to 65% loss of starting material, *none of the anticipated acetone formation* (*via* Norrish Type II fragmentation) *was observed.*

J. Absorption and Emission Data. The λ_{max} and ϵ_{313} values for *trans*- and *cis*-I, as well as model compounds, are presented in Table IV. Examination of the spectra provide no indication of ground state interaction in the γ,δ-unsaturated ketones (contrast, for example, the various "normal" substrates with the β,γ-unsaturated ketone, 4-hexen-2-one).

Table IV. Absorption Data[a]

Ketone	λ_{max} nm (ϵ)	ϵ_{313}
2-Heptanone	281.6 (19.1)	4.6
trans-I	280.8 (24.8)	7.2
cis-I	280.0 (24.7)	5.5
trans-4-Methyl-5-hepten-2-one	283.0 (24.5)	8.4
5-Heptyn-2-one	280.0 (23.0)	5.1
6-Hepten-2-one	281.0 (18.5)	4.4
4-Hexen-2-one	289.5 (65.3)	23.8

[a] All solutions in *n*-hexane.

Room temperature fluorescence data are shown in Table V. The wavelengths at maximum emission are corrected and band areas are given relative to 2-heptanone. *No fluorescence was detected for either trans-I or trans-4-methyl-5-hepten-2-one.*

Table V. Fluorescence Data[a]

Ketone	λ_{max}, nm	Relative area
4-Hexen-2-one	412	4.0
Acetone	412	3.0
2-Heptanone	412	(1.0)
6-Hepten-2-one	399	0.45
5-Heptyn-2-one	412	0.24
trans-4-Methyl-5-hepten-2-one	No fluorescence	
trans-I	No fluorescence	

[a] *n*-Hexane solutions at 25°, all of identical absorbance at the excitation wavelength of 280 nm.

Phosphorescence emission from *trans*-I was detectable in an isopentane glass at 77°K.[27] The emission has a peak maximum at 426 nm with fine structure at 398, 461, and 498 nm. By comparison, phosphorescence from 2-heptanone is unstructured with a λ_{max}

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[21] N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 6974 (1970).

[22] Triplet energy transfer to a higher energy (*e.g.*, mono) olefin (3-methyl-2-pentene) was used by Yang, *et al.* to determine this value, and the data in Table III could be low by as much as 10%. (Reported ϕ_f's for acetone at 25° in solution vary from 0.01[23] to 0.001[24]).

[23] R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

[24] A. M. Halpern and W. R. Ware, *ibid.*, **54**, 1271 (1971).

[25] J. W. Hilpern, G. Porter and L. J. Stief, *Proc. Roy. Soc., Ser. A*, **277**, 437 (1964).

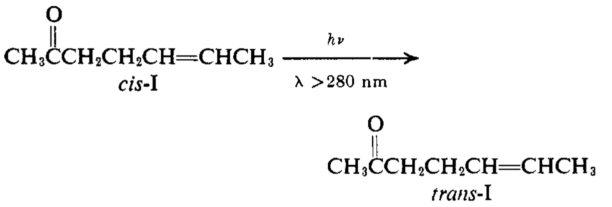
[26] "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Carnegie Press, Pittsburgh, Pa., 1953.

[27] Excessive noise and scatter prevented us from obtaining total emission spectra under these conditions.

at 441 nm. The ratio of areas of the *trans*-I and heptanone emission is 1:5.[28]

Discussion

The results reported herein may be summarized as follows. Both *cis*- and *trans*-5-hepten-2-one (I) undergo photoisomerization ($\lambda > 280$ nm), but whereas *trans*-I leads to both trans–cis isomerization and oxetane (II) formation (eq 4), *cis*-I gives *trans*-I as the only isolable product (eq 5). Both reactions are inefficient



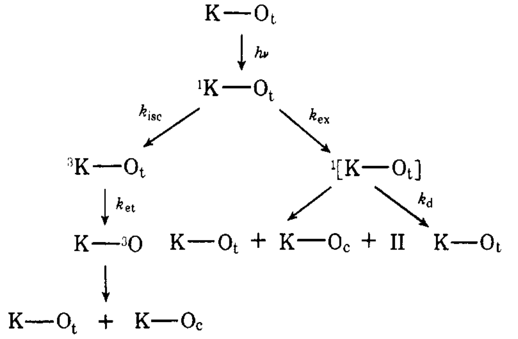
$$\underset{cis\text{-I}}{CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CHCH_3} \xrightarrow[\lambda > 280\ \text{nm}]{h\nu} \underset{trans\text{-I}}{CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH{=}CHCH_3} \quad (5)$$

($\phi_{t\to c}$ 0.02, ϕ_{II} 0.015, $\phi_{c\to t}$ 0.029) and, though the quantum efficiencies for ketone disappearance are somewhat higher than those for observed product formation, it is evident that *unproductive decay of the excited state(s) is the major photochemical process for both isomers.* That photochemistry which is observed is most probably primarily *singlet derived or a consequence of rapid triplet processes*, since oxetane formation is quenched neither by oxygen nor *cis*-1,3-pentadiene, while olefin isomerization is insensitive to oxygen and quenched inefficiently (initial Stern–Volmer slope *ca.* 0.10 ± 0.01 M^{-1} sec^{-1}) and incompletely (limiting value *ca.* 64%) by *cis*-1,3-pentadiene. The difference in the response of oxetane formation and trans–cis isomerization to the presence of 1,3-pentadiene argues for an at least partial divergence in their mode of formation with *cycloaddition a likely consequence of singlet interaction;* the apparent stereospecificity of the addition provides at least circumstantial support for this hypothesis.[29]

In fact, *several pieces of data point toward a minimal amount of intersystem crossing in I, and a much reduced excited singlet lifetime.* Thus, triplet formation was undetectable using a chemical triplet-counting technique sufficiently sensitive for a variety of model systems. The same result has previously been observed for 1-phenyl-2-butene,[3] but in that system phenyl triplets elude detection by rapid and efficient energy transfer to the double bond, where their existence eventually surfaces in the form of high (*ca.* 0.2) quantum efficiencies of cis–trans isomerization. By contrast, cis–trans isomerization of I is quite inefficient, even though ϕ_{isc} for such a ketone might have reasonably been expected to be ≥ 0.3.[21] Thus, diminished triplet formation rather than rapid, internal consumption seems to be involved in 5-hepten-2-one. This conclusion derives striking support from the complete absence of (usually facile) type II decomposition in the photolysis of 4-methyl-5-hepten-2-one.[31] The *complete* absence of type II cleavage in this substrate suggests that not only are triplets not being formed, but that even singlet-derived type II decomposition is unable to manifest itself.[32] The obvious implication is a much reduced excited singlet lifetime for these γ,δ-unsaturated ketones, and this is confirmed by the absence of detectable fluorescence from these compounds. Since the rate constants would be: for fluorescence[24] *ca.* 6×10^5 sec^{-1}, for singlet abstraction of a primary hydrogen[33] *ca.* 2×10^8 sec^{-1}, and for intersystem crossing[21] *ca.* 4×10^8 sec^{-1}, and since there is no reason to believe that these rates are unusually low in the γ,δ-unsaturated ketones, *it would appear that some new singlet process having a rate constant markedly larger than* 4×10^8 *sec*$^{-1}$ *is responsible for the lack of competition from these other phenomena.*

The features discussed above require that *the 5-hepten-2-one system, rather than mirroring the internal triplet transfer characteristics of 1-phenyl-2-butene, actually resembles 6-phenyl-2-hexene*, a molecule in which rapid singlet exciplex formation effectively shortens the singlet lifetime, minimizes intersystem crossing and eventually results in internal cycloaddition.[4] It is of interest that neither of these bichromophoric molecules gives evidence of ground state interaction through perturbation of their absorption spectra; furthermore, the excited state interactions are in both cases apparently reduced at low temperatures in a frozen glass,[34] wherein 6-phenyl-2-hexene fluorescence is observed to increase from minimal intensity to a "normal" value and phosphorescence from 5-hepten-2-one is observable[35] (though reduced in intensity and more highly structured relative to 2-heptanone). A mechanism, analogous to that suggested[4] for the 6-phenyl-2-hexene photolysis, is presented in Scheme I, where K-O represents 5-hepten-2-one in the trans (O_t) or cis (O_c) configurations and the superscripts denote excited state multiplicity localized on one of the nonconjugated

Scheme I



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(28) Excitation spectra were recorded at 298°K and 77°K; they were featureless and showed maximum excitation within 5 nm of the absorption maximum.

(29) Isomeric oxetanes are known to be formed when carbonyl triplets are the precursor species;[30] however, our ignorance of the properties of the (cis) oxetane isomeric with II requires this argument be taken only as suggestive.[16]

(30) D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(31) An identical observation has been made in the 5-norbornenyl systems: R. R. Sauers and K. W. Kelly, *J. Org. Chem.*, **35**, 498 (1970), and private communication.

(32) Both singlet and triplet type II decomposition would have been expected; *cf.* T. J. Dougherty, *J. Amer. Chem. Soc.*, **87**, 4011 (1965); P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965); *ibid.*, **88**, 1245 (1966).

(33) N. C. Yang, S. P. Elliott, and B. Kim, *ibid.*, **91**, 7551 (1969).

(34) An observation analogous to that made by Hirayama (*J. Chem. Phys.*, **42**, 3163 (1963)) for internal excimer formation in 1,3-diphenylpropane, and attributed by Chandross and Demptster through studies of dinaphthylpropane ((*J. Amer. Chem. Soc.*, **92**, 3586 (1970)) to an activation energy for complexation.

(35) Phosphorescence is not observed from 6-phenyl-2-hexene, presumably because those aryl triplets which do form at low temperature rapidly transfer energy to the double bond; such triplet transfer would be likely to be less efficient in the keto olefin.[36]

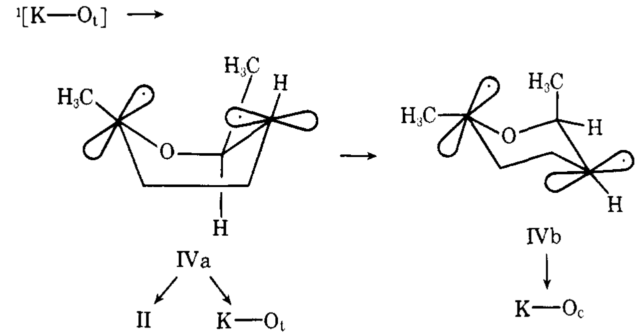
(36) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966).

chromophores or delocalized in the (bracketed) exciplex.

Some comments on this scheme are in order. Formation of oxetanes *via* the ketone excited singlet state and an intermediate exciplex has precedent,[37–39] though its observation in intermolecular systems has required an olefin made particularly electron rich or electron deficient through alkoxy or nitrile substitution. Our observations here suggest that such special electronic requirements may be replaced by an optimal juxtaposition of the reaction moieties, and the recent report[40a] that alkanals react with "normal" olefins through a *singlet* exciplex suggests a more detailed analysis of ketone systems may be justified.[40b] The ability of a second chromophore to internally trap an excited singlet species now seems well established,[41] a separation of three methylene units a seeming requirement in some of the other systems. Two methylenes appear optimum for the keto olefin (*cf.* the fluorescence and ϕ_{isc} data for 6-hepten-2-one) and substitution of an acetylene (5-heptyn-2-one) likewise diminishes the interaction.[42]

The formation of triplet 1,4-biradicals from the reaction of a triplet ketone with an olefin is now commonly acknowledged,[43,44] (a prior complexation seems likely[45,46]), and it has been suggested that analogous singlet biradicals precede formation of the singlet derived oxetanes.[37,39,40] The inclusion of a similar intermediate in Scheme I might allow for an explanation of the *cis*-1,3-pentadiene quenching data, which are suggestive of at least partial trans → cis isomerization through the singlet manifold (*cf.* Scheme II).[47] Because the biradical IVa is likely to be formed with the nonbonded electrons initially orthogonal to one another, conformational inversion could be competitive with cleavage and closure of IVa,[48] with cleavage of the new biradical conformer (IVb) now resulting in net isomerization about the double bond.

Scheme II



To explain the fact that some quenching of olefin isomerization but not oxetane formation occurs upon addition of *cis*-1,3-pentadiene, Scheme I includes an intersystem crossing step and internal triplet energy transfer.[49] The observation of some triplet quenching, by contrast with the 1-phenyl-2-butene system,[3] suggests (not surprisingly) that the intramolecular triplet transfer step is slower for the keto olefin than the aryl olefin (where $k_{et} \geq 4 \times 10^9$ sec^{-1}).

Summary

We conclude that in addition to internal triplet energy transfer (1-phenyl-2-butene)[3] and singlet energy transfer (2-ethoxyethyl phenylacetate),[5] a principal mode of interaction of nonconjugated bichromophoric molecules in the singlet excited state is internal complexation. The net result of such interaction is diminished fluorescence and intersystem crossing, and the introduction of chemical reaction between the interacting moieties. *The most striking aspect of this complexation is its ability to compete with other rapid modes of radiative and radiationless decay* and the geometric and energetic requirements of such complexation are presently under study. The properties peculiar to nonconjugated bichromophoric molecules clearly warrant extensive further investigation.

Experimental Section

Instrumentation. Infrared spectra were recorded on a Beckman IR 8 spectrophotometer; ultraviolet spectra on a Bausch and Lomb 505 or a Cary 14 spectrophotometer using *n*-hexane as solvent; nmr spectra on a Varian A-60 spectrometer with chemical shifts reported in ppm from TMS (δ); mass spectra on a Hitachi-Perkin Elmer RMU-6A mass spectrometer. Microanalyses were by Dr. Yeh of this department.

All quenching or comparative experiments were done using a rotating turntable, Corex tubes, and a 450-W, Hanovia type L mercury arc with associated quartz immersion well and Pyrex filter sleeve. The turntable was set in a constant temperature water bath. In some experiments, the 313-nm line from the arc was isolated using a potassium chromate–potassium hydroxide filter solution.[50] Preparative runs were carried out with a Pyrex photolysis vessel, in which was inserted the 450-W arc and immersion well. Vycor and Corex filter sleeves were used for short-wavelength cut-off. Quantum yield determinations as well as the low temperature and viscosity experiments were done using a Bausch and Lomb high intensity monochromator as previously described,[4b] with the monochromator set at 280 (±24) or 313 (±24) nm. Solvent deoxygenation was routinely employed unless otherwise noted, using argon for 1–1.5 hr. Actinometry was by the uranyl oxalate method.[51] Emission studies were done on a "home-made" spectrophotofluorimeter[52] and are corrected. Fluorescence spectra

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(37) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970), and references therein.

(38) J. A. Barltrop and H. A. J. Carless, *Tetrahedron Lett.*, 3901 (1968).

(39) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970).

(40) (a) N. C. Yang and W. Eisenhardt, *ibid.*, **93**, 1277 (1971). (b) The recent reports of ketone–diene interactions in the singlet state are pertinent: J. A. Barltrop and H. A. J. Carless, *Chem. Commun.*, 1637 (1970); P. Dowd, A. Gold, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5725 (1970); F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *ibid.*, **92**, 1793 (1970).

(41) Reference 4b and references therein.

(42) The reduction in oxetane formation at low temperature may be a consequence of an activation energy for exciplex formation, *cf.* footnote 34.

(43) N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3264 (1968).

(44) J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969).

(45) I. H. Kochevar and P. J. Wagner, *ibid.*, **92**, 5742 (1970).

(46) R. A. Caldwell, G. W. Sovocool, and R. J. Peresie, *ibid.*, **93**, 779 (1971), and references therein.

(47) See reference 39 for a similar report of singlet derived cis–trans isomerization.

(48) Excellent discussions of the relative rates of bond rotation and ring closure may be found in reference 39, R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969) and P. D. Bartlett, *Quart. Rev., Chem. Soc.*, 473 (1970). Other suggestions of conformational isomerism during the lifetime of singlet 1,4 biradicals may be found in W. R. Roth and M. Martin, *Tetrahedron Lett.*, 3865 (1967); L. A. Paquette and J. A. Schwartz, *J. Amer. Chem. Soc.*, **92**, 3215 (1970).

(49) It should be noted that the inefficiency of the quenching and the low quantum efficiency of triplet formation would not have allowed for observable cis-1,3-pentadiene isomerization.

(50) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

(51) G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).

(52) R. B. Brainard, Ph.D. Thesis, Purdue University, Lafayette, Ind., Aug 1970.

were obtained from *n*-hexane solutions and phosphorescence spectra from isopentane or ethanol glasses (77°K).

Vapor phase chromatography (glpc) was done using a Varian-Aerograph A-90-P3 chromatograph with accompanying Leeds and Northrup recorder and disc integrator or with a Varian-Aerograph Hy-Fi Model 600 and associated recorder and disc integrator. Columns used were, in the main, a 25 × 0.125 in. 25% bis(2-(2-methoxyethoxy))ethyl ether column for pentadiene analyses and a a 20 ft × 0.125 in. 5% X F − 1150 column for the heptenones and their photoproducts. The latter column was purchased from Varian-Aerograph and gradually deteriorated with time; neither the company nor we were able to reproduce its efficiency in subsequent attempts. Quantitative analyses were made using *p*-dichlorobenzene as an internal standard. Acetone was analyzed with a 20 ft × 0.25 in. 25% β,β'-oxydipropionitrile column at 55° using methyl ethyl ketone as internal standard.

Solvents. *n*-Pentane was either Phillips Petroleum Co. spectral grade or Burdick and Jackson distilled in glass. The latter was used as received; the former was passed through alumina before use—in either case the solvent was transparent beyond 250 nm. *n*-Hexane was from Burdick and Jackson and used as received (transparent beyond 250 nm). Isopentane was Phillips Petroleum Co. instrument grade and purified by passage through silica (transparent beyond 250 nm). Normal tetradecane was Phillips Petroleum Co. pure grade and purified by washing with concd sulfuric acid followed by chromatography on alumina (transparent beyond 250 nm). Ethanol was dried and distilled prior to its use.

1-Chloro-2-butyne. This material was made using a procedure analogous to that reported[53] for the preparation of 1-chloro-2-heptyne. From 10 g of 2-butyn-1-ol there was obtained 7.7 g (77%) of 1-chloro-2-butyne: bp 28° (24 mm) [lit.[54] 104–106° (760 mm)]; ir (CCl_4), 4.41 μ; nmr (CCl_4), δ 1.84 (t, 3 H), 4.02 (q, 2 H).

5-Heptyn-2-one. This material was made using the general procedure of Crombie, *et al.*[9] From 5.0 g of 1-chloro-2-butyne and 7.45 g of ethyl acetoacetate, there was obtained 4.0 g (64%) of 5-heptyn-2-one: bp 82–83° (25 mm) [lit.[9] 58–63° (10 mm)]. Yields ranged from 47 to 64%. The ketone was purified by preparative glpc (10 ft × 0.375 in. 30% SF-96; 120°): ir (CCl_4), 5.81 μ; nmr (CCl_4), δ 1.70 (t, 3 H), 2.08 (s, 3 H) and 2.44 (m, 4 H); uv (*n*-hexane), λ_{max} 280 nm (ϵ 23).

***trans*-5-Hepten-2-one.** This compound was prepared by the general procedure[9] used for the preparation of 5-heptyn-2-one, with 1-chloro-2-butene substituted for the 1-chloro-2-butyne. Yields were *ca.* 50%: bp 90–92° (102 mm) [lit.[9,55] 148–152° (760 mm), 78–81 (22 mm)]. Purification was accomplished by preparative glpc on a 10 ft × 0.375 in. 30% SF-96 column to give a mixture of cis and trans isomers, followed by the use of a 10 ft × 0.375 in. 10% $AbBF_4$–20% Carbowax 1540 at 95° to isolate the trans isomer (dual chromatography was necessary to prevent decomposition of the $AgBF_4$ column): ir (neat) 5.84 and 10.33 μ; nmr (CCl_4), δ 1.62 (d, 3 H), 2.03 (s, 3 H), 2.32 (m, 4 H), and 5.40 (m, 2 H); uv (*n*-hexane), λ_{max} 281 nm (ϵ 25); mass spectrum, 112 ($M\cdot^{+}$), 43 (base peak) *m/e*. *Anal.* Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.04; H, 10.72.

***cis*-5-Hepten-2-one.** This compound was prepared, with some modification, by the procedure of Crombie, *et al.*[9] Palladium–barium sulfate (0.5 g), absolute methanol (30 ml), and pyridine (5 ml) were added to a reduction flask, the catalyst was prereduced, and 5-heptyn-2-one (5.0 g, 0.046 mol) was added; 879 ml (.078 mol) of hydrogen was absorbed over a 2-hr period. Removal of the catalyst and solvent followed by distillation gave 1.0 g (20%) of the olefinic ketone: bp 89–94° (102 mm) [lit.[9] 43–48° (10 mm)]. Final purification was accomplished on the $AgBF_4$ column: ir (neat), 5.84 and 14.38 μ; nmr (CCl_4), δ 1.62 (d, 3 H), 2.04 (s, 3 H), 2.34 (m, 4 H), and 5.37 (m, 2 H); uv (*n*-hexane), λ_{max} 280 nm (ϵ 25); mass spectrum: 112 ($M\cdot^{+}$), 43 (base peak) *m/e*. *Anal.* Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.81; H, 10.90.

1,3-Dimethyl-2-oxabicyclo[2.2.0]hexane (II). This compound was made on a preparative scale by photolyzing 5.0 g of 5-hepten-2-one (96% trans/4% cis) in 110 ml of *n*-pentane using a 450-W medium pressure Hanovia lamp set in a water-cooled quartz immersion well and Corex filter (cutoff at 260 nm). After 12 hr, the *n*-pentane was carefully distilled at atmospheric pressure using a Vigreux distillation column, and the oxetane was purified by preparative glpc using a 20 ft × 0.25 in., 10% Carbowax-1540 column at 80°: ir (neat), 6.92, 7.28, 8.04, 10.14, 10.47, and 11.07 μ; nmr (CCl_4), δ 1.31 (d, 3 H), 1.33 (s, 3 H), 2.33 (m, 5 H), 4.58 (m, 1 H); mass spectrum, 112 ($M\cdot^{+}$), 43 (base peak) *m/e*. *Anal.* Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.68; H, 10.78.

4-Chloro-2-pentene. 4-Chloro-2-pentene was prepared by the procedure of Arcus and Smith[56] to give 23 g (82%): bp 99–101° (760 mm) [lit.[56] 68° (270 mm)]; ir (CCl_4): 10.43, 15.88 μ; nmr (CCl_4), δ 2.53 (d, 3 H), 2.71 (d, 3 H), 4.42 (m, 1 H), 5.61 (m, 2 H).

***trans*-4-Methyl-5-hepten-2-one.**[57] This compound was prepared by the general procedure[9] used for 5-heptyn-2-one, but 4-chloro-2-pentene was used as the allylic halide and the ketone, rather than being steam distilled, was separated from the aqueous layer during work-up by ether extraction. Evaporation of the solvent gave a crude product (35% yield) which was purified by glpc on the 10 ft × 0.375 in., 30% SF-96 column followed by the 10 ft × 0.375 in. 10% $AgBF_4$–20% Carbowax 1540 column: ir (CCl_4), 5.81, 10.36 μ; nmr (benzene): δ 0.91 (d, 3 H), 1.53 (d, 3 H), 1.73 (s, 3 H), 2.08 (m, 2 H), 2.57 (m, 1 H), 5.31 (m, 2 H); uv (*n*-hexane), λ_{max} 283 nm (ϵ 25); mass spectrum: 126 ($M\cdot^{+}$), 43 (base peak) *m/e*. *Anal.* Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 75.93; H, 11.32.

1-Methylcyclohexanol. This compound was prepared by the procedure of Nevitt and Hammond[58] in 81% yield: bp 61–63° (17 mm) [lit.[58] 68° (24 mm)]; ir (neat), 2.95 μ; nmr (CCl_4), δ 1.16 (s, 3 H), 1.48 (s, 10 H), 2.87 (s, 1 H).

1-Methylcyclohexyl 1-Hydroperoxide.[59] This was prepared by the procedure of Milas and Perry[59] and used without purification in the following procedure.

6-Hepten-2-one. This ketone was prepared by the procedure of De La Mare, *et al.*,[60] to give a crude product containing a mixture of alcohol and ketone. Purification was accomplished on a 10 ft × 0.375 in. 30% DEGS column at 100°: ir (neat), 3.29, 5.85, 6.15, 10.10, and 10.99 μ; nmr (CCl_4), δ 1.77 (m, 4 H), 2.04 (s, 3 H), 2.38 (t, 3 H), and 5.45 (m, 3 H); uv (*n*-hexane), λ_{max} 281 nm (ϵ 19).

Turntable Experiments. All samples for the turntable experiments were prepared in a similar manner. To Corex photolysis tubes, filled with *ca.* 50 ml of solvent and degassed with argon, were added known weights of the ketones, quenchers, sensitizers etc. The volume of the solutions was brought to 50 ml, and the reaction mixtures were photolyzed. After photolysis, *p*-dichlorobenzene was added as an internal standard and 0.1–0.2 μl of solution was analyzed by glpc. Because of space limitations, detailed results of the quenching, sensitizaton, and triplet-counting experiments had to be omitted from this section; the data may be found in the doctoral dissertation of S. A. K.[2]

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(53) M. S. Newman and J. H. Wotiz, *J. Amer. Chem. Soc.*, **71**, 1292 (1949).

(54) M. S. Schechter, N. Green, and F. B. LaForge, *ibid.*, **74**, 4902 (1952).

(55) W. Kimel and A. C. Cope, *J. Amer. Chem. Soc*, **65**, 1992 (1943). The procedure used in this reference gave low yields in our laboratory.

(56) C. L. Arcus and A. W. Smith, *J. Chem. Soc.*, 1748 (1939).

(57) P. Miginiac, *Ann. Chim. (Paris)*, 7, 445 (1962).

(58) T. D. Nevitt and G. S. Hammond, *J. Amer. Chem. Soc.*, **76**, 4124 (1954).

(59) N. A. Milas and L. H. Perry, *ibid.*, **68**, 1938 (1946).

(60) H. E. De La Mare, J. K. Kochi, and F. F. Rust, *ibid.*, **86**, 1437 (1963).