Organic and Biological Chemistry

Intramolecular Triplet Energy Transfer[1,2]

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Abstract: The photochemistry of the following series of compounds containing an acetophenone chromophore and a *trans*-β-methylstyryl chromophore separated by one to four methylene groups was investigated: *trans*-1,4-diphenyl-3-buten-1-one (**1**), *trans*-1,5-diphenyl-4-penten-1-one (**2**), *trans*-1,6-diphenyl-5-hexen-1-one (**3**), and *trans*-1,7-diphenyl-6-hepten-1-one (**4**). The quantum yield for trans–cis isomerization in benzene (3660 Å) was found to be 0.52 ± 0.02 for each compound. Compounds **3** and **4** on photolysis were also found to give type-II cleavage products but with very low quantum efficiencies. The kinetic and spectroscopic data for **2**, **3**, and **4** are consistent with unit efficient triplet energy transfer ($\Phi_{et} = 1$) to the *trans*-β-methylstyryl chromophore followed by cis–trans isomerization of this group. The rate constants for the intramolecular triplet energy transfer in benzene solution have been evaluated from triplet quenching data: (**2**) $k_{et} = 7.2 \times 10^{10}$ sec^{-1}, (**3**) $k_{et} = 1.0 \times 10^{10}$ sec^{-1}, (**4**) $k_{et} = 3.3 \times 10^{9}$ sec^{-1}. On the basis of the rate data in benzene and *tert*-butyl alcohol the exchange mechanism is the most reasonable method of energy transfer in these compounds. The Stern–Volmer quenching curve for **1** in benzene indicates that energy transfer occurs from two different excited states.

Photochemical reactions of organic molecules containing one or more nonisolated chromophores generally arise from the lowest energy excited state of a given multiplicity provided discussion is limited to the condensed phases.[5] This is true regardless of whether higher energy excited states are initially formed by light absorption, intersystem crossing, or sensitization. This generalization is possible because of the rapid rate of energy transfer between high-energy excited states and the lowest energy excited state of a given multiplicity. An obvious question concerning the generality of this energy cascade arises for molecules containing more than one isolated chromophore. Intramolecular singlet energy transfer, as monitored by fluorescence spectroscopy, has been extensively documented and studied.[6–15] Energy transfer efficiencies ranged from 0.3 to 1.0 in the compounds studied. The mechanisms for energy transfer, exchange, and resonance modes have been described by Dexter[16] and Forster.[17] Intramolecular triplet energy transfer, followed by phosphorescence emission[9,12,13,18–20] and by chemical reaction of the triplet energy acceptor portion of the molecule,[21–27] have been studied in much less detail. In some of these cases spectral results indicate the chromophores involved interact to the extent that they can no longer be considered isolated[28] and consequently the process is probably best described as an internal conversion.[12–14,21,24] In other cases,[21a,b] biradical intermediates which either form new compounds (oxetanes, cleavage products) or return to starting material with concomitant isomerization can be involved rather than triplet energy transfer. In addition to these questions, very little rate data have been published[9,19,22] to help understand the intimate details of intramolecular triplet energy transfer. Leermakers, Byers, Lamola, and Hammond[9] concluded that the first-order rate constant for triplet energy transfer from a benzophenone moiety to a naphthylene chromophore separated by one to three methylene groups was greater than 10^{10} sec^{-1}; while

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(1) Photochemical Reactions. VI. Part V: D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, **92**, 6281 (1970).

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(13) J. R. DeMember and N. Filipescu, *ibid.*, **90**, 6425 (1968).

(14) A. A. Lamola, *ibid.*, **91**, 4786 (1969).

(15) R. D. Rauh, T. R. Evans, and P. A. Leermakers, *ibid.*, **90**, 6897 (1968).

(16) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

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(18) D. E. Breen and R. A. Keller, *J. Amer. Chem. Soc.*, **90**, 1935 (1968).

(19) R. A. Keller and L. J. Dolby, *ibid.*, **89**, 2768 (1967); **91**, 1293 (1969).

(20) N. Filipeseu, J. R. DeMember, and F. L. Minn, *ibid.*, **91**, 4169 (1969).

(21) (a) H. Morrison, *Tetrahedron Lett.*, 3653 (1964); (b) *J. Amer. Chem. Soc.*, **87**, 932 (1965).

(22) H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968).

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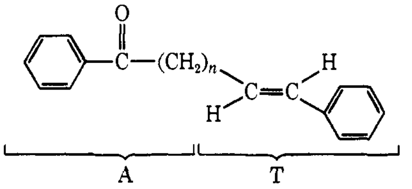
Keller and Dolby[19] obtained rate constants of 25 and 0.04 sec^{-1} for triplet energy transfer from benzophenone and carbazole to naphthylene separated by a rigid steroid bridge (15-Å separation). Morrison and Peiffer[22] obtained a rate constant of 2.0×10^8 sec^{-1} for energy transfer between benzene and butene[29] separated by a single methylene group.

We wish to report several cases of intramolecular triplet energy transfer between carbonyl and olefin chromophores[27] and to provide the first set of rate constants for this process in a series of structurally related compounds. In this series of compounds the acetophenone and *trans*-β-methylstyryl chromophores are separated by one–four methylene groups.

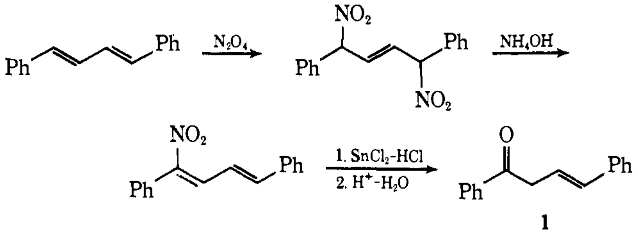


1, $n = 1$
2, $n = 2$
3, $n = 3$
4, $n = 4$

Results

Synthesis of Enones 1–4. The syntheses of the nonconjugated enones utilized in this study are outlined in Charts I–IV. *trans*-1,4-Diphenyl-3-buten-1-one (n = 1) was synthesized by a modification of the method of Wieland.[30] Thus, N_2O_4 was added to 1,4-diphenyl-1,3-butadiene in a 1–4 fashion and the resulting dinitroolefin was treated with ammonium hydroxide. 1,4 elimination of 1 mol of nitrous acid regenerated the original unsaturated system and the resulting nitrodiene was reduced with $SnCl_2$–HCl. The reduction presumably leads to the oxime of the desired enone which is hydrolized *in situ* to **1**. The double bond is assigned the trans stereochemistry both on the basis of ir and nmr spectral data (see Experimental Section) and chemical behavior.[31]

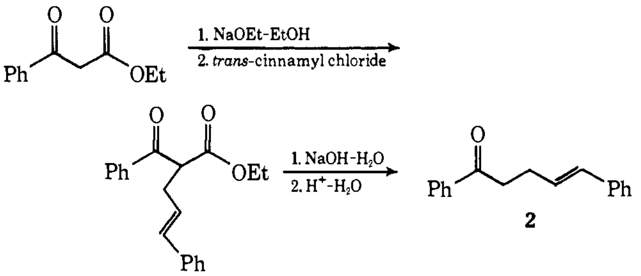
Chart I. Synthesis of **1**



1

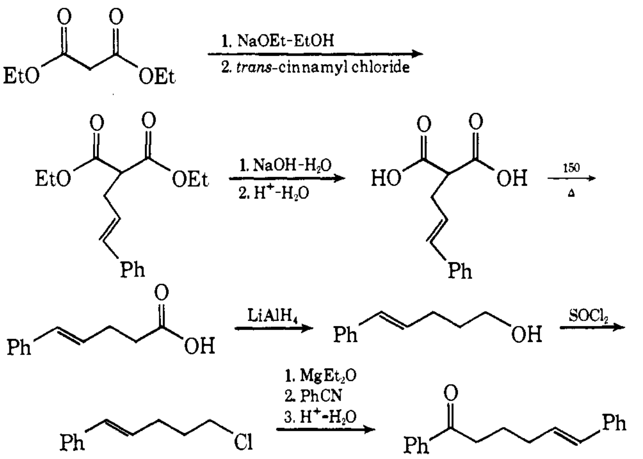
trans-1,5-Diphenyl-4-penten-1-one (n = 2) was synthesized by alkylation of ethyl benzoylacetate with *trans*-cinnamyl chloride followed by saponification and decarboxylation of the resulting substituted β-keto ester. As before, the trans stereochemistry was assigned on the basis of spectral data. The compound was shown to consist of only one isomer by glpc analysis on two different columns each of which was able to separate the cis and trans modifications of this compound.[32]

Chart II. Synthesis of **2**



The synthesis of *trans*-1,6-diphenyl-5-hexen-1-one (n = 3) was initiated with the alkylation of diethyl malonate with *trans*-cinnamyl chloride. The resulting substituted malonic ester was saponified, and the diacid was thermally decarboxylated. The *trans*-styrylpropionic acid thus formed was reduced to the corresponding alcohol with lithium aluminium hydride; treatment of this alcohol with thionyl chloride afforded *trans*-1-phenyl-5-chloropentene-1. This material was converted to the Grignard reagent and allowed to react with benzonitrile. Hydrolysis of the resulting ketimine salt gave n = 3 in good yield. The trans stereochemistry was assigned on the basis of spectral data, and the presence of only one isomer was demonstrated by glpc analysis.

Chart III. Synthesis of **3**



3

The most convenient synthesis of *trans*-1,7-diphenyl-6-hepten-1-one (n = 4) was that due to Zimmerman and English[33] and involved the acid-catalyzed 1,3 elimination of 1-phenyl-2-(hydroxybenzyl)cyclohexanol. This diol was formed by the addition of phenylmagnesium bromide to the aldol condensation product of cyclohexanone and benzaldehyde. It should be noted that the product of the acid-catalyzed cleavage reaction was not characterized by the above investigators. Proof of structure was obtained in our investigation from ir, nmr, uv, and mass spectral data as well as comparison with material synthesized by two other methods as indicated in Chart IV.

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[29] Morrison in a private communication has indicated that this value must be revised inasmuch as some singlet quenching of the excited phenyl group by added piperylene has been observed.

[30] H. Wieland and H. Stenzel, *Chem. Ber.*, **40**, 4825 (1907).

[31] A. Padwa, D. Crumrine, R. Hartman, and R. Layton, *J. Amer. Chem. Soc.*, **89**, 4435 (1967).

[32] After this work was completed an alternate synthesis of n = 2 was published: A. Padwa, E. Alexander, and M. Niemcyzk, *ibid.*, **91**, 456 (1969).

[33] H. E. Zimmerman and J. English, Jr., *ibid.*, **76**, 2285 (1954).

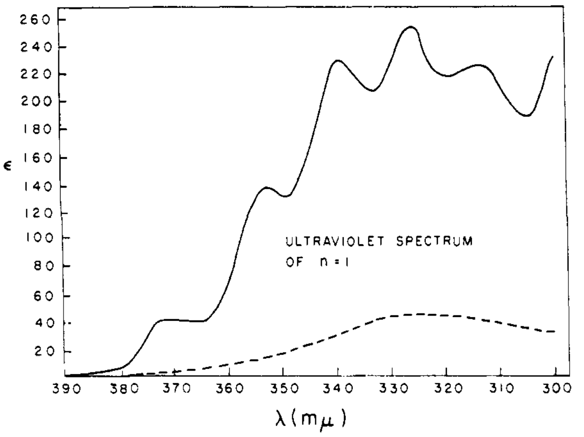


Figure 1. Ultraviolet spectrum (n–π* region) of (a) *trans*-1,4-diphenyl-3-buten-1-one (solid line); (b) equal molar mixture of acetophenone and *trans*-β-methylstyrene (dotted line).

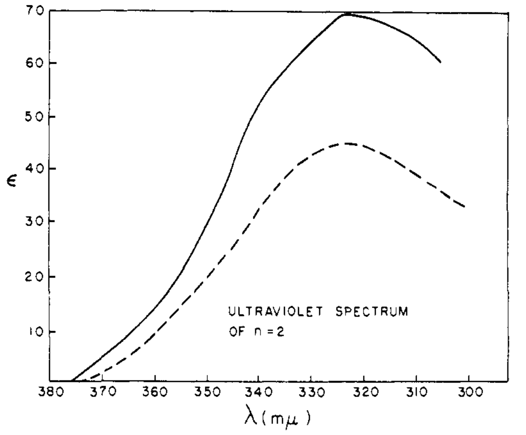


Figure 2. Ultraviolet spectrum (n–π* region) of (a) *trans*-1,5-diphenyl-4-penten-1-one (solid line); (b) equal molar mixture of acetophenone and *trans*-β-methylstyrene (dotted line).

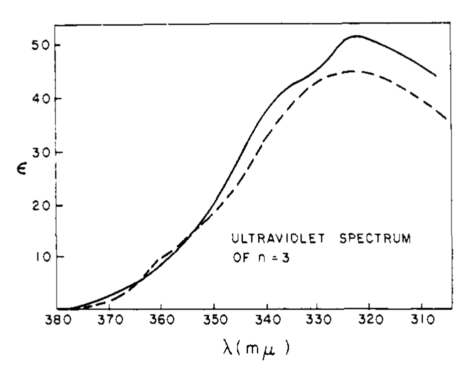


Figure 3. Ultraviolet spectrum (n–π* region) of (a) *trans*-1,6-diphenyl-5-hexen-1-one (solid line); (b) equal molar mixture of acetophenone and *trans*-β-methylstyrene (dotted line).

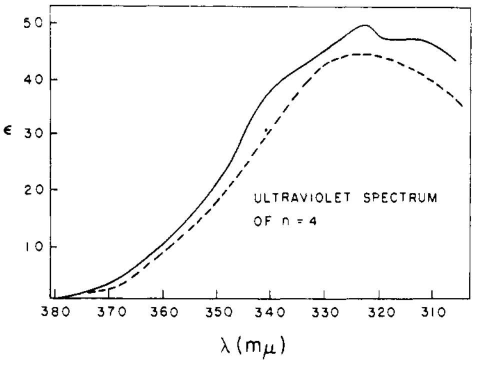
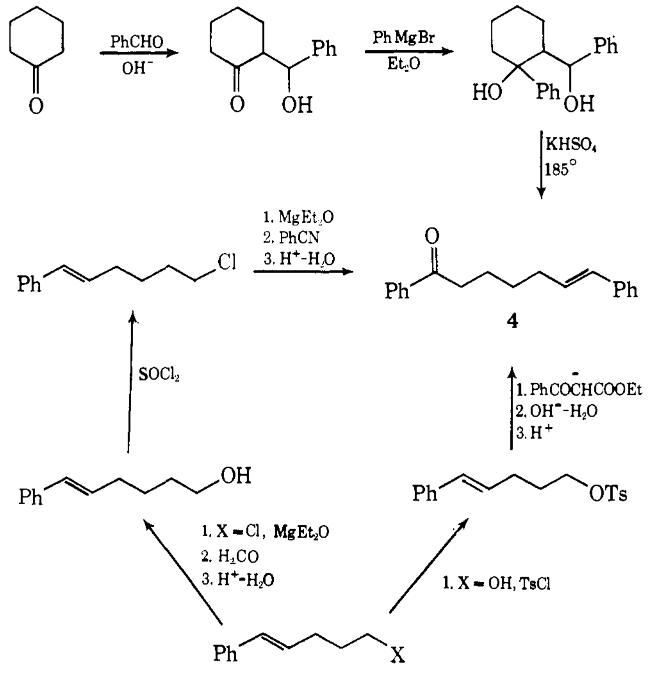


Figure 4. Ultraviolet spectrum (n–π* region) of (a) *trans*-1,7-diphenyl-6-hepten-1-one (solid line); (b) equal molar mixture of acetophenone and *trans*-β-methylstyrene (dotted line).

Ultraviolet Spectra. The n–π* regions of the absorption spectra of compounds **1–4** are shown in Figures 1–4 together with the spectrum of an equimolar solution of acetophenone and *trans*-β-methylstyrene. The two major features to be noted are the coincidence of the positions of the maxima for each member of the series with those of the reference spectrum, the marked hyperchromicity ($\epsilon_{\max}^{n-\pi^*}$ enhanced by a factor of 6), and vibrational fine structure ($\Delta\bar{\nu}$ = 1500 cm^{-1}) of the n–π* band in **1**.[34]

Chart IV. Synthesis of **4**



Photochemical Behavior of Enones 1–4. The results of irradiation of compounds **1–4** with light of wavelengths greater than 3130 Å are shown in Chart V. In the case of *n* = 2–4 the preparative scale photolysis solutions were separated and analyzed by gas chromatography and the structures of the products were assigned on the basis of spectral data and/or comparison with authentic samples. The two unidentified materials detected in the *n* = 4 photolysis mixtures more than likely correspond to the isomeric 1-phenyl-1,4-pentadienes, the formation of which is indicated by the presence of acetophenone after photolysis. In support of this is the similarity of the vpc behavior of these materials and the phenylbutadienes found in the *n* = 3 photolysis mixtures. Analysis of the *n* = 1 photolysates was done by 100-MHz nmr and infrared spectroscopy. Provided photolysis was not continued for extended periods of time, tlc gave only one spot with an R_f value equal to that of the starting material even though ir and nmr clearly showed the disappearance of the trans starting material and concomitant appearance of the cis enone. However, under extended periods of photol-

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(34) More detailed information can be obtained: A. A. Baum, Ph.D. Thesis, The Johns Hopkins University, Baltimore, Md., 1968.

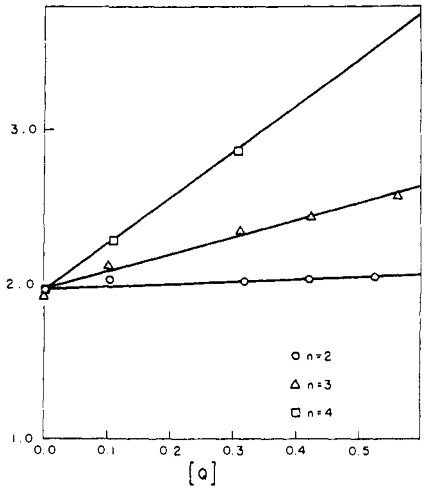
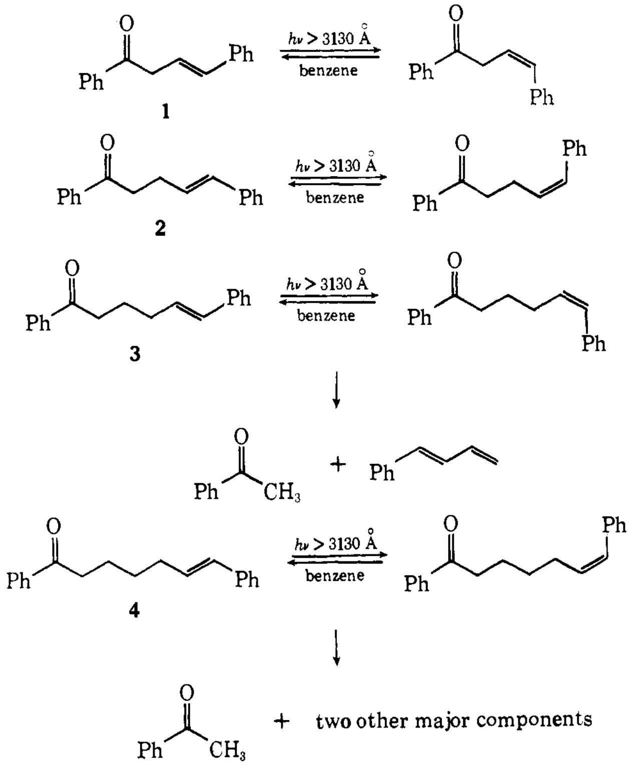


Figure 5. Quenching of trans → cis isomerization of **2**, **3**, and **4** by *trans*-β-methylstyrene (benzene).

ysis, *i.e.*, 3 ml of a 0.022 *M* solution photolyzed for 9 hr, a second spot was observed on tlc. No attempt was made to characterize this material.

Chart V. Photochemistry of **1**, **2**, **3**, and **4**



The results of quantitative studies of the photochemistry of n = 1–4 are shown in Tables I–III.

The quantum yield for trans–cis isomerization of each enone was measured as a function of added *trans*-β-methylstyrene concentration, and the results are presented graphically in Figures 5–7 and summarized in Table IV.

Discussion

In order to qualitatively understand the photochemistry of the nonconjugated enones of this study it is necessary to first consider the relative dispositions of the energies of the various excited states of these compounds. The ultraviolet absorption spectra of these materials (Figures 1–4) show that the singlet energies of both the acetophenone and styryl chromophores are the same as in the parent (isolated) compounds. In

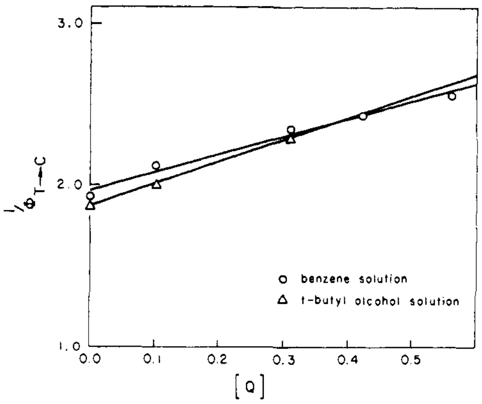


Figure 6. Quenching of trans → cis isomerization of **3** by *trans*-β-methylstyrene (○, benzene; △, *tert*-butyl alcohol).

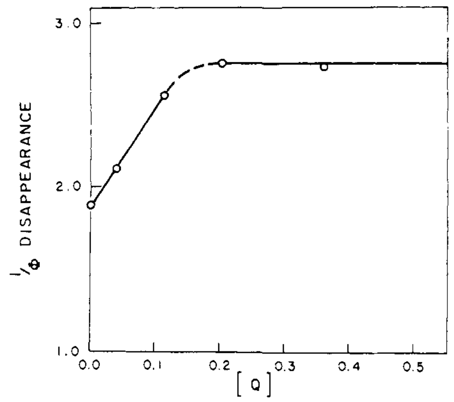


Figure 7. Quenching of trans → cis isomerization (disappearance of 965-cm^{-1} ir band) by *trans*-β-methylstyrene.

Table I. Cis Enone at Photoequilibrium[a] and Quantum Yield[c] for Trans–Cis Isomerization

Compd, n =	% cis at photo-equilibrium	$\Phi_{t\rightarrow c}$[c]
1	53[b]	0.53 ± 0.02[d]
2	52[e]	0.52 ± 0.02[e]
3	59[e,f]	0.52 ± 0.02[e]
4	58[e,f]	0.51 ± 0.02[e]

[a] Benzene solutions photolyzed with light of wavelength greater than 3100 Å. [b] Determined by 100-MHz nmr analysis. [c] Photolysis with λ = 3660 Å; light intensity measured by ferrioxalate actinometry (see Experimental Section). [d] Determined by quantitative infrared analysis. [e] Determined by vpc analysis. [f] Not true photoequilibrium values (see Discussion).

Table II. Relative Importance of Trans–Cis Isomerization and Acetophenone Formation[a]

Compd, n =	Max time to photo-equilibrium	Time of photolysis	% remaining enone which is cis	% theor amt aceto-phenone
3	<90 min	3 hr[c]	59	10
4	<1 hr	65 min[d]	58	10

[a] *I.e.*, type II cleavage; in n = 3 and 4.[b] [b] Benzene solutions photolyzed with light of wavelength greater than 3100 Å. [c] A solution (3.0 ml) initially 0.020 *M* in enone was photolyzed. [d] A solution (3.0 ml) initially 0.024 *M* in enone was photolyzed.

Table III. Photoequilibration of Trans $n = 2$ with and without Added *trans*-β-Methylstyrene[a]

Concn, $n = 2$, M	Vol of soln irrad, ml	Concn *trans*-methylstyrene, M	Photolysis time, hr	Cis $n = 2$, %	*cis*-β-Methylstyrene, %
0.01	400	0.00	3.25	51	
0.01	400	0.00	8.0	52	
0.10	6	0.10	13.0	53	4

[a] Benzene solutions photolyzed with light of wavelength greater than 3100 Å.

Table IV. Stern–Volmer Parameters for $n = 2$–4[a]

Compd, n	Slope[b]	Intercept[b]
2[c]	0.138 ± 0.086	1.97 ± 0.03
3[c]	1.09 ± 0.09	1.97 ± 0.03
3[d]	1.38 ± 0.10	1.87 ± 0.03
4[c]	2.95 ± 0.006	1.959 ± 0.001

[a] Photolysis was with 3660-Å light. [b] Least-squares values. [c] Benzene solution. [d] *tert*-Butyl alcohol solution.

the case of $n = 1$ the increased intensity of the n–π^* absorption strongly indicates some type of interaction between the two chromophores (*vide infra*); however, this interaction apparently does not perturb the singlet energy of either chromophore. Since there is no *a priori* reason to expect that the singlet–triplet splittings should be any different in the "double molecules" than in the isolated chromophores, their triplet energies should likewise be the same as those of the parent compounds.[35,36] This situation is depicted in Figure 8. The enhanced oscillator strength of the n–π^* transition in $n = 1$ represents a general characteristic of the uv spectra of β,γ-unsaturated ketones in which the π orbitals of each chromophore are not fixed in a parallel orientation.[37] There have been two theories advanced to account for this phenomenon: a, the n–π^* transition borrows intensity from an intramolecular charge-transfer transition believed to exist in the appropriately oriented β,γ-unsaturated ketones;[38] and b, n–π^* intensity is borrowed directly from the π–π^* transition.[39] A complete CNDO calculation including configuration interaction seems to best support the latter proposal to the extent that the calculated spectra of several β,γ-unsaturated ketones match the observed spectra almost perfectly.[40] This interpretation also nicely accommodates the kinetic results obtained for $n = 1$. The same considerations may apply in the case of $n = 2$, but in this case the effect is clearly much less important.

The above argument implies that the electronic systems of each chromophore in $n = 2$–4 are essentially independent, noninteracting entities, while the excited singlet states of $n = 1$ are actually admixtures of n–π^* and π–π^* states. As a consequence it is easiest to consider the photochemistry of $n = 2$–4 as a group, and then to treat $n = 1$ as a special case. With the former group of compounds we believe that excitation of the n–π^* singlet is followed by very rapid and completely efficient intersystem crossing to the n–π^* triplet. In support of this it should be noted that Hammond and Wagner[41] have shown that type II elimination such as that observed in the present cases of $n = 3$ and $n = 4$ occurs only from the n–π^* triplet state of phenones, presumably owing to the extremely rapid rate of intersystem crossing in these compounds. The large endothermicity of an n–π^* to π–π^* singlet energy transfer process makes it unlikely that this could effectively compete with intersystem crossing. The triplet states thus produced may now dissipate their excitation energy in three different ways: (1) γ-hydrogen abstraction to initiate the type II photoelimination sequence; (2) intersystem crossing to the ground state; and/or (3) energy transfer to the β-methylstyryl chromophore. The absence of acetophenone in the $n = 2$ photolysis solutions indicates that γ-hydrogen abstraction is unimportant in this case in which the γ-hydrogens are of the vinyl type. This either reflects the relative inertness of vinyl-type hydrogens to abstraction by the electron-deficient carbonyl oxygen of the n–π^* triplet, or the inability of this process to efficiently compete with the very rapid energy-transfer process in $n = 2$ (*vide infra*). The former explanation seems appealing in view of the photostability of otherwise photoreducible ketones in benzene solution. γ-Hydrogen abstraction in the cases of $n = 3$ and 4 does occur although it appears to compete very inefficiently with energy transfer as may be seen from the data of Table II. The observed selectivity of the n–π^* triplet of the carbonyl chromophore in the abstraction of a γ-hydrogen atom (*i.e.*, vinyl *vs.* aliphatic) is striking and may well reflect an activation energy for this photoprocess.[42]

The photoreactivity of $n = 2$–4 is represented in the kinetic sequence of Chart VI, where A-T and A-C are the trans and cis enones, respectively; superscripts 1 and 3 refer to singlet and triplet states, respectively; A-p corresponds to the common triplet intermediate resulting from the transfer of triplet excitation from the acetophenone chromophore to the styryl chromophore

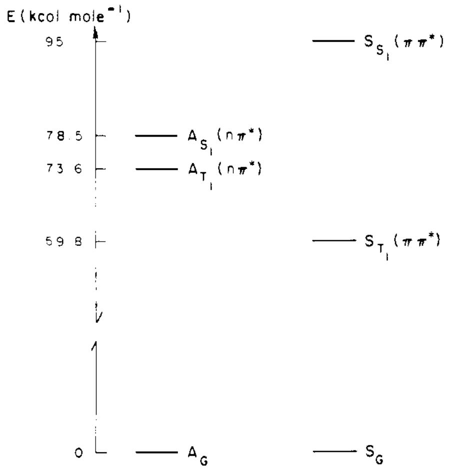


Figure 8. Energy-level diagram for a noninteracting enone (acetophenone and *trans*-β-methylstyrene).

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(35) A. A. Lamola, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1965.

(36) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 297.

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(38) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, p 167.

(39) D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. B*, 215 (1967).

(40) Private communication of J. Del Bene.

(41) P. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

(42) H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969).

Chart VI. Kinetics of the Photochemistry of $n = 2$–4

$$\text{A-T} \longrightarrow \text{A}^1\text{-T}$$

$$\text{rate}(1) = \frac{I_a \epsilon_T[\text{A-T}]}{\epsilon_T[\text{A-T}] + \epsilon_c[\text{A-C}]} \tag{1}$$

$$\text{A}^1\text{-T} \xrightarrow{k_{isc}} \text{A}^3\text{-T} \tag{2}$$

$$\text{A}^3\text{-T} \xrightarrow{k_{eT}} \text{A-p} \tag{3}$$

$$\text{A}^3\text{-T} \xrightarrow{k_d} \text{A-T} \tag{4}$$

$$\text{A}^3\text{-T} \xrightarrow{k_{3I}} \text{products resulting from } \gamma\text{-hydrogen abstraction} \tag{5}$$

$$\text{A-C} \longrightarrow \text{A}^1\text{-C}$$

$$\text{rate}(6) = I_a \frac{\epsilon_c[\text{A-C}]}{\epsilon_T[\text{A-T}] + \epsilon_c[\text{A-T}]} \tag{6}$$

$$\text{A}^1\text{-C} \xrightarrow{k_{isc}'} \text{A}^3\text{-C} \tag{7}$$

$$\text{A}^3\text{-C} \xrightarrow{k_{et}'} \text{A-p} \tag{8}$$

$$\text{A}^3\text{-C} \xrightarrow{k_d'} \text{A-C} \tag{9}$$

$$\text{A}^3\text{-C} \xrightarrow{k_{3II}'} \text{products resulting from } \gamma\text{-hydrogen abstraction} \tag{10}$$

$$\text{A-p} \xrightarrow{k_c} \text{A-C} \tag{11}$$

$$\text{A-p} \xrightarrow{k_T} \text{A-T} \tag{12}$$

of either the cis or trans enone;[43] k_{II} refers to the abstraction of a γ-hydrogen; products resulting from γ-hydrogen abstraction are the appropriate dienes, acetophenone, the appropriate cyclobutanols in the case of $n = 4$, the cyclobutanols and cyclohexanols in the case of $n = 3$,[44] and the starting enones.[45]

It should be noted that Chart VI neglects any possibility of bimolecular energy transfer from A^3-T or A^3-C to A-T or A-C. This omission is justified on the basis of the data of Table III and Figure 5 from which it is seen that when *trans*-β-methylstyrene was present in the photolysis solutions in equimolar quantities with the enones, the amount of energy transfer to it as measured either by the amount of isomerized β-methylstyrene, the quenching of isomerization of the enone, or both is negligible. Under these circumstances, bimolecular energy transfer to the enone and *trans*-β-methylstyrene should occur at the same rate; it can be seen that this process is unimportant at these concentrations. Equations 5 and 10 are not applicable to the case of $n = 2$. In this latter case, analysis of the appropriate equations of Chart VI show that the fraction of cis $n = 2$ in the photoequilibrated mixtures is given by eq 13.[46] In

$$\frac{[\text{A-C}]_{\text{pss}}}{[\text{A-T}]_{\text{pss}} + [\text{A-C}]_{\text{pss}}} = \frac{k_c \phi_{et} \epsilon_T}{k_c \phi_{et} \epsilon_T + k_T \phi_{et} \epsilon_C} \tag{13}$$

this expression, the subscript, pss, refers to "photostationary state," ϵ_C and ϵ_T are the effective molar absorptivities of the cis and trans enones, respectively, and ϕ_{et} and ϕ_{et}' are the efficiencies of energy transfer in the trans and cis enones given by eq 14 and 15. Since

$$\phi_{et} = k_{et}/(k_{et} + k_d) \tag{14}$$

$$\phi_{et}' = k_{et}'/(k_{et}' + k_d') \tag{15}$$

the optical density of a solution of photoequilibrated $n = 2$ at wavelengths greater than 3000 Å is the same as that of the unphotolyzed trans material, ϵ_T must equal ϵ_C for the wavelengths absorbed in these photolyses, and eq 13 reduces to eq 16. Equations 1–4 and 11 and

$$\frac{[\text{A-C}]_{\text{pss}}}{[\text{A-C}]_{\text{pss}} + [\text{A-T}]_{\text{pss}}} = \frac{k_c \phi_{et}}{k_c \phi_{et} + k_T \phi_{et}'} \tag{16}$$

12 of Chart VI show that the quantum yield for trans–cis isomerization is given by eq 17. Since for $n = 2$

$$\Phi_{T\rightarrow C} = \phi_{et}[k_c/(k_c + k_t)] \tag{17}$$

the fraction of cis enone present at photoequilibrium is equal to the trans–cis quantum yield—*i.e.*, eq 16 = eq 17, it follows that $\phi_{et} = \phi_{et}' = 1$, provided the proposed mechanism is correct. In support of these findings, $k_c/(k_c + k_t)$ for β-methylstyrene triplets has been measured[43] and found to equal 0.51 ± 0.01, in excellent agreement with our value as determined by these two methods. The good agreement probably reflects the energetic and geometric similarity between the triplet state of β-methylstyrene and the styryl chromophore triplet in $n = 2$ as well as $n = 3$ and 4 (*vide infra*).

A steady-state kinetic analysis of the complete sequence outlined in Chart VI shows that for $n = 3$ and 4 where eq 5 and 10 must be considered, the fraction of cis isomer found after extended photolysis does not bear the same significance as in the case of $n = 2$. Thus, γ-hydrogen abstraction slowly and irreversibly "drains off" the enone making a true photoequilibration impossible. Accordingly, the corresponding values in column 2 of Table I are not equal to the value of $k_c/(k_c + k_t)$ as was the case for $n = 2$. In these cases, however, the trans–cis quantum yield is still given by eq 17 with a slight change in the definition of ϕ_{et}—*i.e.*

$$\phi_{et} = k_{et}/(k_{et} + k_d + k_{II}) \tag{18}$$

Since the value of the isomerization quantum yield is the same for these compounds as for $n = 2$, it follows that within the limits of experimental error $\phi_{et} = 1$ for $n = 3$ and 4 also. That is, since $\Phi_{T\rightarrow C} = k_c/(k_c + k_t)$ then Φ_{et} must equal unity.

For each compound, $n = 1$–4, the pseudophotostationary state isomer ratio ($[\text{A-T}]/[\text{A-C}])_{\text{pss}}$ was less than one. In those cases where competing reactions are not important the isomer ratio (α) is 0.91. This ratio is a reflection of the rate ratio k_T/k_c. Radical equilibration of $n = 1$–4 and equilibration with low-energy sensitizers which are thought to operate *via* Schenck biradical intermediates produce mixtures where the trans isomer strongly predominates. This indicates that biradical intermediates are not involved in the direct photolysis of these compounds and that isomerization is the result of electronic energy transfer.[47]

Recognition of the fact that the energy transfer efficiency is unity for $n = 2$–4 makes interpretation of the quenching data (Table IV and Figures 5 and 6) straight-

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

(44) A. Padwa and D. Eastman, *J. Amer. Chem. Soc.*, **91**, 462 (1969).

(45) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

(46) The intersystem crossing quantum efficiencies Φ_{isc} and Φ_{isc}' have not been included inasmuch as Chart VI gives only one deactivation path for the triplets. If another path is included in the scheme then the resulting conclusion is that $\Phi_{et}\Phi_{isc} = \Phi_{et}'\Phi_{isc} = 1$.

(47) J. Saltiel, K. R. Newberger, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 3658 (1969).

Table V. Rates and Rate Ratios for Intramolecular Triplet Energy Transfer in **2**, **3**, and **4**

Compd	$\Phi_{et}\Phi_{isc}{}^{a}$	k_q/k_{et}, M^{-1}	k_{et}, sec$^{-1\,b}$
2	0.99	0.069	7.2×10^{10}
3	0.99	0.55	1.0×10^{10}
4	0.98	1.5	3.3×10^{9}

[a] Calculated from $\Phi_{T\to C}(1 + \alpha)$, where $\alpha = k_T/k_c = 0.91$. The decay ratio, α, was determined from the photoequilibrium ([trans]/[cis])$_{pss} = \alpha$. A similar calculation for **1** gives a value of 1.01; this indicates that for this compound every photon absorbed produces an excited state from which isomerization can occur. [b] Assuming k_q(benzene) $= 5 \times 10^{9}$ M^{-1} sec^{-1}.

forward. Thus, the Stern–Volmer equation which describes these systems is given by eq 19, and the slope

$$\frac{1}{\Phi_{T\to C}} = \frac{k_c + k_T}{k_c}\left(1 + \frac{k_q}{k_{eT}}[Q]\right) \qquad (19)$$

divided by the intercept gives the ratio of k_q/k_{et}. Table V shows the results for $n = 2$–4 in benzene solution.[48]

The detailed mechanism for the intramolecular energy transfer process must be able to account for the 1.2-order of magnitude decrease in k_{et} in going from $n = 2$ to $n = 4$. An inspection of molecular models shows that on the average the distance between the two chromophores remains nearly constant in the compounds in question. However, the number of conformations in which the two ends of the molecule are nearly in contact decreases greatly with increasing number of methylene groups. Furthermore, the data in Table IV and Figure 6 show that in *tert*-butyl alcohol solution k_q/k_{et} has a value of 0.75 in the case of $n = 3$ as compared to the value of 0.55 in benzene solution. Since the solvent properties of *tert*-butyl alcohol are quite different from those for benzene (for example, the viscosities at 23° are a factor of 10 different[51]), this shows that k_{et} depends to the same extent on these properties as does k_q. The logical conclusion to be drawn from these considerations is that in $n = 2$–4, intramolecular triplet energy transfer occurs by the same mechanism as bimolecular quenching—namely by the exchange mechanism which requires a collision between the donor and acceptor.

The special case of $n = 1$ must now be considered. As with the other members of the series, the quantum yield for trans–cis isomerization[35] indicates that in the absence of quencher the energy transfer efficiency is unity; however, the quenching data of Figure 7 clearly demonstrate that the mechanism is not that outlined in Chart VI. More specifically, these data are consistent with the isomerization occurring from two different excited states one, of which is quenchable and one of which is not. This behavior can be understood in terms of the interpretation given to the uv spectrum of this material; that is, the absorption band appearing in the usual position of the n–π^* absorption is in an admixture of n–π^* and π–π^* states. Thus, excitation in this absorption band instantaneously introduces some singlet energy into the β-methylstyryl chromophore. If intersystem crossing from this singlet state generates two triplet states, neither of which is an admixture, rather either n–π^* or π–π^*, then the π–π^* triplet formation by this path would be nonquenchable. The n–π^* triplet, on the other hand, would be expected to transfer its energy with unit efficiency in the absence of quencher, while in the presence of quencher intramolecular energy transfer would have to compete with bimolecular quenching. While this explanation affords a qualitative understanding of the data, it does not account for the relative ease with which the n–π^* triplet component can be quenched. This is particularly troublesome when compared to the insensitivity to quenching of triplet energy transfer in $n = 2$. For this and other reasons this explanation must be regarded as tentative; more work on this system is planned.

In summary, it appears that in compounds (**2**, **3**, and **4**) where the uv spectra indicate that the two chromophores are essentially noninteracting, triplet energy transfer occurs by a diffusion-limited exchange mechanism. In the case of **1**, where the uv spectrum indicates considerable mixing of states an alternate energy transfer mechanism becomes operative.

Experimental Section

General. All melting points reported in the following sections were obtained on a Thomas-Hoover Model 6406-H melting point apparatus equipped with a thermometer calibrated against standard samples. Normal boiling points were uncorrected for variations in atmospheric pressure and were, for the most part, measured with uncalibrated thermometers. The pressures reported along with reduced pressure boiling points were measured with an R. G. I. Swivel McCloud gauge.

Gas–liquid partition chromatography results were obtained on an Aerograph Hi-Fy Model 600-D instrument equipped with a flame ionization detector and a Leeds-Northrop Speedomax-W 10 millivolt recorder equipped with a Model 224-4 disk integrator.

Routine infrared spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer. Analytical infrared work was done on a Perkin-Elmer Model 527 grating instrument. Solution-phase spectra were run with matched sodium chloride cells. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. Nuclear magnetic resonance spectra were recorded on either a Varian Model A-60 or a Varian Model HA-100 nmr spectrophotometer as indicated.

Wherever possible, reagent grade solvents were used in synthetic procedures and these were distilled as a matter of course. In most instances, liquid organic reagents were distilled and solids were recrystallized and dried under vacuum prior to use. Photolyses were performed either in benzene distilled from sodium and stored over molecular sieves or in distilled *tert*-butyl alcohol as indicated.

Photolysis Apparatus. Preparative or qualitative irradiations were performed with a Hanovia 450-W medium-pressure mercury-arc lamp along with a uranium-glass cut-off filter which transmitted light of wavelengths greater than 313 nm. The lamp and filter were contained in either a quartz or Vycor water-cooled jacket. In some experiments, the lamp, filter, and jacket were immersed in the reaction well containing the solution to be irradiated. In these instances, Seaford-grade nitrogen was bubbled continuously through the solution during the course of the irradiation. Stirring was effected by means of a Teflon-coated magnetic stirring bar. In other instances, solutions to be photolyzed were placed in small Pyrex test tubes (generally, 3 ml of solution per test tube). These were degassed by the freeze–pump–thaw method (4 cycles, 0.002 mm) and placed in a cylindrical adapter which fit around the water-jacketed lamp and filter. An electrical blower installed in the bottom of the adapter ensured the flow of cool air. In all cases, a steady flow of room temperature water circulated through the cooling jacket during an irradiation.

Quantitative runs were performed on an optical bench consisting of a lamp, lamp housing, and a series of carriers holding filters, the

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(48) An efficient singlet quenching by dienes has been observed for aromatic hydrocarbons[49] and alkyl but *not* aryl ketones.[50] Inasmuch as intersystem crossing is several orders of magnitude faster in aryl ketones, singlet quenching is not likely under our reaction conditions.

(49) L. M. Stevenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968).

(50) F. S. Weltack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1793 (1970).

(51) For experimental estimates of diffusion rate constants in tertiary alcohols, see P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968). Wagner concludes that the diffusion rate constant in *tert*-butyl alcohol is somewhat larger than would be calculated from the viscosity.

reaction cell, and a phototube, and housing mounted on a calibrated carriage all firmly secured to a 2-m long triangular steel rail. The lamp employed was a Hanovia-Engelhard 1000-W Hg-Xe compact-arc lamp. The lamp housing contained a 4-in. spherical mirror (F/1.2) ground from fused quartz and coated with aluminum and MgF_2. The reflectance at 200 nm was 85%. This was positioned behind the lamp in such a way as to focus the radiation from the source on a 1- or 2-nm circular slit positioned one focal length behind a 4-in. quartz lens (F/1.2) mounted in a movable barrel which was secured to the front of the housing. A baffle was secured to the inside of the housing so as to prevent direct radiation from the source from falling on the slit. The slit lay along the optical axis defined by the collecting mirror and collimating lens. To minimize spherical aberration a stop of 1.5-in. diameter was routinely used. After emerging from the housing, radiation impinged upon Corning filters C.S.-737 and O-52 which isolated the 366-nm mercury line.[52]

The 2.9-cm long cylindrical photolysis cell with quartz windows 44.5 mm in diameter rested in a machined cell holder situated between the filter holder and a calibrated carriage upon which was mounted an RCA-935 phototube in a housing with an adjustable iris diaphragm. The calibrated carriage allowed the phototube to be moved laterally across or out of the beam and then to be returned to the initial position with great precision. Finally, a plane mirror making an angle of 45° with the horizontal was situated behind the carriage so that light emerging from the rear window of the cell when the phototube was not in position was deflected out of the optical path.

***trans*-1,4-Diphenyl-3-buten-1-one (1).** A slight modification of the method of Wieland and Stenzel[30] gave, in one typical run, 22% overall yield of *trans*-1,4-diphenyl-3-buten-1-one, mp 90–91°, after recrystallization from absolute ethanol.[53]

***trans*-1,5-Diphenyl-4-penten-1-one (2).** To 300 ml of absolute alcohol in a 1-l. three-necked flask fitted with a reflux condenser, mechanical stirrer, and adding funnel was added 11.7 g (0.51 mol) of sodium under a nitrogen atmosphere. After the sodium dissolved, the solution was allowed to cool to 30° and 98 g (0.51 mol) of freshly distilled ethyl benzoylacetate was added dropwise with stirring. After addition of the benzoylacetic ester was complete, 76.5 g (0.5 mol) of cinnamyl chloride[54] was added dropwise with stirring as the solution was heated to reflux. By the end of the addition, the solution was refluxing gently, and the presence of sodium chloride precipitate was noted. The mixture was allowed to cool to room temperature and stand for 12 hr after which the ethanol was removed at reduced pressure. The residue was partitioned between ether and water, the layers were separated, and the aqueous layer was extracted three times with ether. The combined ether extracts were dried over anhydrous $MgSO_4$, and the ether was removed under reduced pressure. The residue, without further purification, was dissolved in 1500 ml of 0.727 *N* alcoholic NaOH solution (8 g of NaOH:250 ml of 95% EtOH:25 ml of H_2O) and stirred for 10 hr. The temperature rose to 35° during the saponification. After saponification the solution was cautiously made just acidic with 50% H_2SO_4. Carbon dioxide was rapidly evolved and stirring was continued for 12 hr. The slightly acidic solution was then extracted thoroughly with ether and the ether extract was washed twice with sodium bicarbonate solution and then water before drying over anhydrous $MgSO_4$. The ether was removed under reduced pressure and the remaining solid was recrystallized from petroleum ether (30–60°) giving 59.7 g (50.5%) of a white solid: mp 59.5–60°; uv max (cyclohexane) 324 (ϵ 68), 248 nm (ϵ 27,800); ir ($CHCl_3$) 1690, 965, 690 cm^{-1}; 100-MHz nmr (CCl_4) τ 7.47 (2 H, quartet, $J = 7$ Hz), 7.06 (2 H, triplet, $J = 7$ Hz), 3.78 (2 H, AB part of ABX_2 signal, $J_{AB} = 15$ Hz, $J_{BX} = 7$ Hz, $J_{AX} = 0$ Hz), 2.80 (8 H, complex), 2.17 (2 H, complex). *Anal.* Calcd for $C_{17}H_{16}O$: C, 86.50; H, 6.75. Found: C, 86.42; H, 6.79.

***trans*-1-Phenyl-4-carboxy-1-butene.** To a solution of 146 g of KOH in 167 ml of H_2O was added 135 g (0.5 mol) of cinnamylmalonic acid diethyl ester which had been prepared according to the method of Barnard and Bateman.[55] The addition was made slowly with stirring at room temperature. The mixture rapidly became homogeneous, but stirring was continued for an additional 2 hr. The solution was then heated to boiling to ensure complete reaction. After cooling, the solution was made acidic with 12 *N* HCl and the resulting mixture was extracted with ether. After drying the ether extracts over anhydrous $MgSO_4$, the ether was evaporated under reduced pressure and the remaining solid was heated to 160° on an oil bath with stirring until no more CO_2 was evolved from the melt. The contents of the flask were cooled to room temperature and recrystallized from light petroleum–benzene to give 64.0 g (73%) of the white crystalline acid: mp 88–89°; ir ($CHCl_3$) 3020, 1720, 965, 692 cm^{-1}. *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.28; H, 6.95.

***trans*-1-Phenyl-1-penten-5-ol.** In a 2-l. three-necked flask equipped with a reflux condenser, adding funnel, and mechanical stirrer were placed 38.2 g of $LiAlH_4$ and 500 ml of dry ether.

trans-1-Phenyl-4-carboxy-1-butene (117.5 g) in 500 ml of dry ether was then added carefully at room temperature with stirring. After addition, the mixture was heated to reflux for 36 hr. The mixture was then cautiously poured onto ice and enough 12 *N* HCl was added to dissolve all the remaining solid material. The ether layer was separated and the aqueous layer was thoroughly extracted with ether. The combined ether layers were dried over anhydrous $MgSO_4$ and the ether was removed. The oily residue was distilled to give 100.5 g (92.5%) of a colorless liquid: bp 98°; ir ($CHCl_3$) 3610, 3440, 3013, 2940, 1500, 965, 692 cm^{-1}. *Anal.* Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.03; H, 8.62.

***trans*-1-Phenyl-5-chloro-1-pentene.** Thionyl chloride (48 ml) was added slowly to a stirred solution of pyridine (59 ml distilled from CaO) and chloroform (65 ml), cooling being effected by an ice bath. The thionyl chloride–pyridine solution was then transferred to an addition funnel and added to a stirred solution of *trans*-1-phenyl-1-penten-5-ol (91.5 g) in $CHCl_3$ (65 ml) at room temperature with stirring. After addition the solution was heated at reflux for 5 hr. The dark solution was then extracted four times with H_2O and twice with 3 *N* HCl. The $CHCl_3$ extracts were dried ($CaCl_2$) and the chloroform was removed at reduced pressure. The oily residue was distilled to give 80.0 g (79%) of a colorless liquid: bp 86° (0.05 mm); ir (neat) 3020, 2950, 2930, 1595, 1490, 1440, 1295, 963, 735, 961 cm^{-1}. *Anal.* Calcd for $C_{11}H_{13}Cl$: C, 73.13; H, 7.25. Found: C, 73.10; H, 7.08.

***trans*-1,6-Diphenyl-5-hexen-1-one (3).** Magnesium turnings (2.82 g, 0.116 g-atom) were placed in a 500-ml three-necked flask fitted with a reflux condenser, mechanical stirrer, and adding funnel. The apparatus was heated with a yellow flame to expel moisture and then allowed to cool under a stream of dry N_2. After the flask had cooled to room temperature, a small crystal of I_2 was introduced into the flask along with 15 ml of anhydrous ether. The mixture was then inoculated with 2.0 g of *trans*-1-phenyl-5-chloro-1-pentene. When reaction commenced (as evidenced by the refluxing solvent) an additional 18 g of the chloroolefin dissolved in 105 ml of dry ether was added with stirring under N_2 over a 1.5-hr period. The reaction mixture was then allowed to stir at room temperature for an additional 2.5 hr. After this time, 9.16 g (0.089 mol) of freshly distilled benzonitrile was added in a dropwise fashion and the resulting cloudy mixture was stirred under reflux for 24 hr. HCl (40 ml. 12 *N*) and 13 ml of H_2O were then added slowly and the mixture was stirred under reflux for an additional 36 hr. Enough water was then added to dissolve the white solid material which formed during hydrolysis, and the ether and aqueous layers were separated. The aqueous layer was thoroughly ether extracted and the combined ether extracts were washed first with saturated $NaHCO_3$ solution and then with water. After drying on anhydrous $MgSO_4$, removal of the solvent at reduced pressure afforded a solid residue which was recrystallized from petroleum ether (30–60°) to give 17.26 g (78% based on benzonitrile) of a solid: mp 53.5–54.5°; uv max (cyclohexane) 324 (ϵ 51), 245 nm (ϵ 2800); ir (CCl_4) 3030, 2930, 1690, 1460, 1223, 965, 690 cm^{-1}; 60-MHz nmr (CCl_4) τ 2.1–2.9 (10 H, complex), 3.83 (2 H, AB part of ABX_2 multiplet, $J_{AB} = 16$ Hz), 7.18 (2 H, triplet, $J = 7$ Hz), 8.00 (4 H, multiplet); 100-MHz nmr (CCl_4) τ 8.14 (2 H, quintet, $J = 7$ Hz), 7.76 (2 H, quartet, $J = 7$ Hz), 7.13 (2 H, triplet, $J = 7$ Hz), 3.80 (2 H, AB part of ABX_2 signal, $J_{AB} = 15$ Hz, $J_{BX} = 7$ Hz, $J_{AX} = 0$ Hz), 2.78 (8 H, complex), 2.14 (2 H, complex). *Anal.* Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.36; H, 7.02.

2-(α-Hydroxybenzyl)cyclohexanone. This material was prepared in 57% yield according to the method of Bellimoravia,[56] mp 99–100°.

***trans*-1,7-Diphenyl-6-hepten-1-one (4).** This material was most conveniently prepared from 2-(α-hydroxybenzyl)cyclohexanone ac-

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(52) Hanovia-Engelhard specifications show that radiation emitted from the Hg–Xe compact arc lamp consists primarily of the mercury line spectrum superimposed on a weak continuum.

(53) For spectral characteristics of *trans*-1,4-diphenyl-3-buten-1-one see ref 31.

(54) H. Gilman and S. A. Harris, *Recl. Trav. Chim. Pays-Bas*, **50**, 1052 (1931).

(55) D. Barnard and L. Bateman, *J. Chem. Soc.*, 926 (1950).

(56) J. D. Bellimoravia, *ibid.*, 1126 (1955).

Table VI. Per Cent Total Ion Current of Some Ions in the Mass Spectra of Compounds **1–4** at 70 eV

	M$^+$	M − 91	M − 120	133	120	117	115	105	91	77
1	5.4 (*m/e* 222)					3.0	3.6	60.2	1.8	10.8
2	21.5 (*m/e* 236)	1.7	1.4			5.2	2.8	34.7	4.2	6.6
3	7.4 (*m/e* 250)		32.0		2.6	2.2	6.1	6.1	2.9	7.7
4	8.9 (*m/e* 264)	3.7	4.2	10.0	8.9	4.7	2.8	13.1	3.1	6.0

cording to the method of Zimmerman and English.[33] The yield was 14% based on the amount of 2-(α-hydroxybenzyl)cyclohexanone used in the first step: bp 170° (0.05 mm); uv max (cyclohexane) 324 (ϵ 50), 248 nm (ϵ 26,000); ir (neat) 3070, 3050, 3020, 2925, 2850, 1690, 1600, 1580, 1498, 1455, 1410, 1375, 1360, 1312, 1249, 1217, 1191, 1178, 1069, 1000, 963, 745, 690 cm^{-1}; 100-MHz (CCl$_4$) τ 2.10 (2 H, complex), 2.76 (8 H, complex), 3.77 (2 H, AB part of ABX$_2$ signal, J_{AB} = 15 Hz, J_{BX} = 6 Hz, J_{AX} = 0 Hz), 7.11 (2 H, triplet, J = 7 Hz), 7.76 (2 H, quartet, J = 6 Hz), 8.23 (4 H, multiplet). *Anal.* Calcd for C$_{19}$H$_{20}$O: C, 86.32; H, 7.63. Found: C, 86.38; H, 7.58.

Product Studies. (a) Photolysis of *trans*-1,5-Diphenyl-4-penten-1-one (n = 2). *trans*-1,5-Diphenyl-4-penten-1-one (0.945 g) was dissolved in 400 ml of dry benzene (0.01 *M* solution) and the solution was irradiated through uranium glass for 3.25 hr. An identical solution was irradiated for 8 hr under the same conditions. After photolysis, the solvent was removed under vacuum leaving 0.950 g of an oil which crystallized in the deep freeze (mp 32–38°).

The material proved to be homogeneous on both alumina and silica gel tlc developed with a variety of mixtures of benzene and pentane, and had an R_f identical with that of the starting material in each case. These results were identical with those obtained with the 8-hr photolysis solution. The ir spectrum of the photolysis mixture was identical with that of the trans starting material with the exception that the 965-cm^{-1} band had considerably diminished in intensity relative to the other bands in the spectrum.

Samples of each photolysis mixture were injected onto a glpc column (2.5% Apiezon-L on silinized Chromosorb G) at 205°. In addition to the starting trans compound (retention time 16 min) one other peak was observed in each case (retention time 11 min). The per cent of the shorter retention time material present as measured by the relative peak areas was 51.0 ± 5% (3 hr) and 54.4 ± 0.5 (8 hr). The same percentages were obtained on a 2.5% Carbowax 20M on Chromosorb G column operating at 222°. It should be noted that on each column the relative peak areas were independent of the injector temperature over a 60° range and that the trans isomer was homogeneous on both columns under the conditions reported above.

A small amount of the 8-hr photolysis mixture was dissolved in benzene along with a crystal of I$_2$. After 5 days the solution was extracted with 0.1 *N* Na$_2$S$_2$O$_3$, washed with water, dried on CaCl$_2$, and injected onto a 2.5% Apiezon-L on Chromosorb G silinized glpc column at 205°. The shorter retention time material now comprised only 17% of the binary mixture.

The 100-MHz nmr spectrum[34] of the irradiated material showed the mixture contained only cis and trans n = 2.

(b) Photolysis of *trans*-1,5-Diphenyl-4-penten-1-one in the Presence of an Equimolar Quantity of *trans*-β-Methylstyrene. A solution (6 ml; 0.119 g) of freshly distilled *trans*-β-methylstyrene and 0.236 g of *trans*-1,5,-diphenyl-4-penten-1-one in 10 ml of benzene (0.1 *M* in each component) was placed in a Pyrex test tube and degassed at 0.002 mm. The tube was sealed under vacuum and the solution was irradiated for 13 hr through uranium glass. Glpc analysis of the photolysate was performed on a 5% Carbowax 20M on Chromosorb G column at two different temperatures. At 203°, the β-methylstyrene came off with the solvent and the cis and trans isomers of n = 2 were found to be present in a ratio of 53:47. When the material from the photolysis was injected onto the column at 120°, the cis and trans isomers of β-methylstyrene were well separated from the solvent peak and found to be present in a ratio of 4:96.

(c) Photolysis of *trans*-1,6-Diphenyl-5-hexen-1-one. *trans*-1,6-Diphenyl-5-hexen-1-one (1.09 g) was dissolved in 200 ml of benzene (0.02 *M*). This solution was irradiated under N$_2$ for 5.4 hr through uranium glass. After irradiation, the solvent was removed and the residue was chromatographed on silica gel using a petroleum ether–benzene–ether eluent system. A total of 0.87 g of material was collected in three separate bands.

The first material eluted was shown to be a mixture of *cis*- and *trans*-1-phenylbutadiene by spectral and glpc comparison with the authentic material.[57]

The material in the second band had a 100-MHz nmr spectrum[34] consistent with a mixture of *cis*- and *trans*-1,6-diphenyl-5-hexen-1-one and an ir spectrum identical with that of the starting material with the exception of the fact that the 965-cm^{-1} band was of diminished relative intensity. Gas-chromatographic analysis of this material on a 1% Carbowax 20M on silinized Chromosorb G column operating at 202° showed two materials present in a ratio of 1.4:1. The less abundant, long retention time material had the same retention time (13 min) as authentic trans n = 3. The other (cis) component had a retention time of 9 min. The relative peak intensities were insensitive to changes in the injection port temperature over a 55° range. The trans isomer was homogeneous on glpc under these conditions.

The material in the third band was not homogeneous on tlc. Careful rechromatography on silica gel developed with 90% benzene–10% pentane showed that the mixture contained more than 90% of one material which was identical with an authentic sample of acetophenone (ir, nmr, and glpc comparison).

When 3 ml of a 0.02 *M* solution of *trans*-1,6-diphenyl-5-hexen-1-one was irradiated for 3.0 hr and the reaction mixture was analyzed by standard glpc methods, it was found to contain 10% of the theoretically possible amount of acetophenone and 90% of the theoretical amount of the mixture of *cis*- and *trans*-1,6-diphenyl-5-hexen-1-one.

When benzene solutions (0.01 *M*) of *trans*-1,6-diphenyl-5-hexen-1-one were irradiated such that conversion to the cis isomer did not exceed 12% (*vide infra*) no other products could be detected by glpc analysis.

(d) Photolysis of *trans*-1,7-Diphenyl-6-hepten-1-one. When benzene solutions (0.02 *M*) of *trans*-1,7-diphenyl-6-hepten-1-one were photolyzed as in the case of n = 3 (*vide supra*) and the photolysate was chromatographed on silica gel, three major bands were isolated as in the previous case. Infrared analysis of the first band showed that this contained only hydrocarbon material. The second band contained a mixture of cis and trans isomers of the starting material in a cis–trans ratio of 57:43%. This was determined by glpc analysis on a 2.5% Apiezon-L on Chromosorb G silinized column operated at 235°. The retention time of the cis isomer was 12.5 min; that of the trans material was 18 min. The same ratio was obtained on a 1% Carbowax 20M column operating at 220°. The ratio was independent of the injection port temperature and the trans starting material was homogeneous on either column under these conditions. Nmr analysis (100 MHz) verified that this material consisted of only cis and trans isomers of 1,7-diphenyl-6-hepten-1-one.

The third chromatographic band was shown to contain acetophenone by comparison with an authentic sample.

When 3 ml of a benzene solution of *trans*-1,7-diphenyl-6-hepten-1-one was photolyzed for 65 min and then quantitatively analyzed by standard glpc methods it was found to contain 10% of the theoretically obtainable amount of acetophenone and 90% of the theoretical amount of cis and trans isomers of the starting material (cis–trans = 1.4:1).

As in the case of n = 3, when solutions of trans n = 4 were irradiated such that a maximum of 15% of the material was converted to the cis isomer, no other products (*e.g.*, acetophenone) could be detected by glpc analysis.

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(57) O. Grummitt and E. Becker, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., pp 771–775.

(e) Photolysis of *trans*-1,4-Diphenyl-3-buten-1-one. A solution (3.0 ml) of 0.0486 g of trans $n = 1$ diluted to 10 ml with benzene (0.0218 M in $n = 1$) was placed in each of three 10 × 75 mm Pyrex test tubes. The tubes were degassed at 0.002 mm, sealed under vacuum, and photolyzed for different lengths of time: solution I, 5 min; II, 1 hr; III, 9 hr.

After photolysis, the solvent was removed under vacuum and the residues were examined by tlc analysis (silica gel developed with benzene).

Solutions I and II proved to show only one spot on tlc. This spot had the same R_f value as the starting material.

Solution III showed two distinct spots on tlc; the slower moving of the two components had the same R_f value as the starting material.

Attempts to analyze these solutions on the vpc failed owing to on-column decomposition of the enone, and, presumably, the photoproducts. This decomposition was noted on several different columns—*i.e.* Apiezon-L, Carbowax 20M, diethylene glycol succinate, and SE-30.

The infrared spectrum of the photolyzed product from solution I was taken and found to be nearly superimposable with that of the starting material. The main difference between the two spectra was that the 965-cm^{-1} band in the photolyzed material showed a much diminished intensity relative to the other peaks of the spectrum compared with that band in the spectrum of the starting material.

The 100-MHz nmr spectrum of a sample of 50 mg of *trans*-1,4-diphenyl-3-buten-1-one dissolved in 3 ml of benzene which had been irradiated for 0.5 hr showed that a mixture of cis and trans isomers of the starting material was present in a ratio of 53:47%. No other products could be detected.

Quantum Yield Determinations in the Case of n = 2–4. The lamp was started and allowed to warm up for about 45 min after which the intensity at 366 nm was determined by potassium ferrioxalate actinometry.[36] The actinometry was performed in the same cell and under precisely the same conditions which were used for photolysis of the enones. In experiments in which no quencher was used, the photolysis cell was then filled with solvent (either benzene or *tert*-butyl alcohol as indicated) and placed in the cell holder. The phototube was then placed in a known position behind the cell and the iris was opened to a known diameter. A reading (I_0) was taken on a Simpson #269 Triplet meter, operating in the 16 μA range, which was connected in series with the phototube and a 120-V battery. After the photolysis solution had been degassed the filled cell was replaced in the cell holder and the timer was started. A second phototube reading was taken (I) and the phototube was moved out of the beam. The photolysis was then allowed to proceed. After each 0.5 hr the timer was stopped, the solution was well shaken, and the light intensity was monitored with the phototube. Little or no change in the phototube response was noted during any irradiation. From the relative phototube responses, the fraction of light absorbed by the reactant was computed—*i.e.*, $f_A = 1 - (I/I_0)$.

In runs employing quencher (*trans*-β-methylstyrene) the optical density of the photolysis solutions at 366 nm was measured in a 1-cm cell. This value was multiplied by 2.9 cm to obtain the optical density of the solutions when in the photolysis cell. Since the *trans*-β-methylstyrene exhibited a small but measurable absorbance at 366 nm (ϵ 0.09), the fraction of the light absorbed by the enone was computed from the total optical density and the known concentrations and extinction coefficients of the enone and β-methylstyrene, as shown below. A and B refer to the enone and *trans*-β-methylstyrene, respectively.

$$f_A = \left(1 - \frac{1}{\log^{-1} \mathrm{OD}}\right)\frac{\epsilon_A C_A}{\epsilon_A C_A + \epsilon_B C_B}$$

After photolysis the solution in the cell was thoroughly mixed and transferred to a 100-ml round-bottomed flask. The solvent was removed under vacuum and the residue was dissolved in between 3 and 5 ml of reagent acetone. The resulting solution was analyzed on glpc for per cent cis enone. The quantum yield for trans–cis isomerization was then computed from the following expression, where V is the volume of solution in the cell, F is the fraction of cis enone present after photolysis, c is the concentration of enone in the photolysis solution, I_a is the intensity absorbed by the actinometer solution (photons/second), f_a is the fraction of incident light absorbed by the enone, and t is the time in seconds. Standard error analyses using empirically determined uncertainties indicate that the quantum yields are reliable to 4%.

$$\Phi_{t\rightarrow c} = \frac{VF_c}{I_a f_A t} \times 6.02 \times 10^{23}$$

The results are presented in Figures 5 and 6 and Tables I and IV.

Quantum Yield Determinations in the Case of n = 1. Due to the large extinction coefficient of this material at 366 nm, a 0.02 M solution in a 2.9-cm cell absorbed >99% of the light. Thus, the fraction of light absorbed by the enone in solutions containing some quencher is

$$f_A = \frac{\epsilon_A C_A}{\epsilon_A C_A + \epsilon_B C_B}$$

where A and B refer to $n = 1$ and quencher, respectively. With the exception of this modification, the irradiation procedure was the same as described above. After irradiation the solutions were quantitatively transferred to 100-ml round-bottomed flasks. The solvent was removed in a stream of N_2, and the flasks were evacuated to 0.02 mm and warmed for 2 hr in order to remove the β-methylstyrene. The solid residues were dissolved in CCl_4, transferred to 10- or 25-ml volumetric flasks, and diluted to volume with CCl_4. The per cent transmittance at 965 cm^{-1} was then measured on a Perkin-Elmer Model 521 infrared spectrophotometer which had been calibrated against known samples of trans $n = 1$. The least-squares calibration curve showed that concentration was related to optical density by the following equation: $c = {}^1/_{1.72}(\mathrm{OD} + 0.0002)$. The least-squares slope is accurate to better than 1%. Matched 0.1-mm sodium chloride cells were used for work, and CCl_4 was placed in the reference beam.

After determining the concentration of trans $n = 1$ remaining, the number of moles remaining was calculated and from this value together with the known initial number of moles, the disappearance quantum yield was computed as follows, where V_1 is the volume of the photolysis solution of initial trans enone concentration c_1, V_2 is the volume of the ir solution of concentration c_1, and the other symbols have their usual meaning. The results are presented in Figure 7 and Table I.

$$\Phi_{\text{disappearance}} \cong \Phi_{t\rightarrow c} = \frac{V_1 c_1 - V_2 c_2}{I_a f_A t} \times 6.02 \times 10^{23}$$