

ACCOUNTS OF CHEMICAL RESEARCH

VOLUME 12

NUMBER 11

NOVEMBER, 1979

Photochemistry of Organic Bichromophoric Molecules

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Received April 20, 1979

In recent years organic photochemistry has matured to the stage where the consequences of excitation of the more common chromophores (i.e., benzene, ketone, ester, olefin, halogen, nitro, etc.) are reasonably well (though by no means completely!) understood. It is therefore logical that the next level of complexity be broached—the photochemical consequences of irradiating molecules containing two or more functional groups.^{1,2}

Such has been our concern for the last decade as we have systematically explored interchromophoric interactions in polyfunctional molecules. Functional group pairs which have been studied include aryl-olefin, aryl-acetylene, aryl-ester, aryl-amide, aryl-chloride, aryl-ketone, keto-olefin, and benzoyl-olefin. Interactions in the ground state, as well as in either (or both) of the excited singlet or triplet manifolds, have been observed, with photophysical as well as photochemical consequences. Though this aspect of organic photochemistry is still a young science, it is already obvious that these effects may be so profound as to completely dominate a molecule's excited-state properties. Clearly a general knowledge of interchromophoric interactions, including the dependence of these interactions on the separation and relative orientation of the functionalities, is a necessary prerequisite to a predictive capability for even modestly complex organic structures.

Our approach to this area has involved two different classes of molecules: (1) bifunctional acyclics which are relatively free of conformational constraints and thus have available a wide range of pre- and postexcitation stereochemical relationships and (2) well-defined cyclic substrates which allow a study of the dependence of photophysical and photochemical phenomena on chromophore geometry. In both cases, we have routinely characterized the ground state and lowest lying singlet and triplet states of the substrates using absorption (plus, more recently, photoelectron spectroscopy), fluorescence (wavelength, efficiency, lifetime), and phosphorescence (wavelength, efficiency) spectroscopy, respectively. By these means, we attempt to ascertain qualitatively the degree to which excitation may be

considered "localized" on a target chromophore and the extent to which one or both of the excited states is perturbed. However, it is recognized that considering a particular bichromophoric molecule as having "isolated" chromophores is, at best, an approximation. The degree of interaction can be expected to span a wide range, with the "isolated" and "completely mixed" characterizations at the extremes of the scale. There is thus good reason to speak in terms of a molecule having a particular set of spectral characteristics associated with which are a concomitant set of photochemical and photophysical properties, rather than attempting to label the chromophore as such.

In this Account we outline our observations with several substrates from each of three bichromophore systems. Our work on nonconjugated aryl-olefins is the most advanced and is taken up first. This is followed by a discussion of some keto- and benzoyl-olefins, and finally some aryl-esters. These several combinations nicely exemplify many of the phenomena we and others have uncovered to date. We stress that our approach has been basically phenomenological; this field has been virtually ignored by theoreticians and is ripe for approach from this direction.³

Nonconjugated Aryl-Olefins⁴

The excited singlet state of a simple alkylbenzene is normally characterized by a set of competing photophysical processes⁵ which includes *fluorescence*, which is return to the ground state with emission of a photon (rate = k_f , efficiency = ϕ_f), *radiationless decay* to the ground state (k_{ic} , ϕ_{ic}), and *intersystem crossing* to the triplet state (k_{isc} , ϕ_{isc}). Once in the triplet state, the aromatic may return to the ground state, again either with emission of a photon (*phosphorescence*) or by dissipation of the triplet energy as heat without emis-

(1) Leading references may be found in (a) F. Scully, T. Nylund, F. Palensky, and H. Morrison, *J. Am. Chem. Soc.*, **100**, 7352 (1978); R. G. Weiss and G. S. Hammond, *ibid.*, **100**, 1172 (1978).

(2) F. C. DeSchryver and N. Boens, *Adv. Photochem.*, **10**, 359 (1977).

(3) Zimmerman has recently developed an approach using calculated bond orders in the ground and singlet excited states to define the "excited" portion of a molecule; cf. H. E. Zimmerman and T. R. Welter, *J. Am. Chem. Soc.*, **100**, 4131 (1978); H. E. Zimmerman, M. G. Steinmetz, and C. L. Kreil, *ibid.*, **100**, 4146 (1978).

(4) For an overview, see H. Morrison, *Org. Photochem.*, **4**, in press.

(5) For an excellent introduction to photochemical terminology and concepts, see N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings Inc., Menlo Park, CA, 1978.

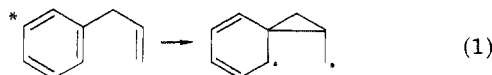
Harry Morrison was born and raised in Brooklyn, New York. His undergraduate training was at Brandeis University (B.A., 1957) and his Ph.D. was received from Harvard University. After postdoctoral stints at the Eidgenössische Technische Hochschule in Zurich and at the University of Wisconsin, he joined the Purdue faculty in 1963 and is now Professor of Chemistry.

Table I
Summary of Spectral Data for 1-Phenyl-2-butene (1)
Relative to Toluene (2) or 1-Phenylbutane (3)⁷

type of spectroscopy	principal observations
absorption	long wavelength (¹ B _{2u}) transition virtually superimposable on that of 2; end absorption red-shifted by ca. 5 nm
photoelectron ⁹	1: 8.75, 9.25 eV; 3: 8.69, 9.22 eV
fluorescence	emission superimposable on that of 3, with 1, $\phi_f = 0.11$, $^1\tau = 26$ ns; 3, $\phi_f = 0.11$, $^1\tau = 30$ ns
phosphorescence	no phosphorescence from 1; phosphorescence from 2 and 3 is readily observable (EtOH glass) under conditions such that intermolecular quenching does not occur

sion of light (another intersystem-crossing event).

Upon introduction of a double bond into the alkylbenzene, one or more of at least five modes of intramolecular aryl-olefin excited-state interactions may compete with the above phenomena.⁴ For the aryl singlet, there is evidence for (1) formation of a *charge-transfer state*, with charge either donated to or received from the aryl excited singlet by the olefin ground state, and (2) formation of an excited complex ("*exciplex*")⁵ involving ground-state olefin and the aryl excited singlet. (Exciplexes usually favor a coplanar arrangement of the two interacting groups and also involve, to some degree, a charge-transfer contribution to stabilization of the complex.) Once formed, the aryl triplet state ($E_T \sim 83$ kcal/mol) may (3) internally transfer triplet excitation to the olefin ($E_T \sim 76$ kcal/mol) (via an orbital overlap dependent "exchange" mechanism)⁵ or (4) undergo a rapid, *olefin-induced radiationless decay* back to the ground state. Finally, both the aryl singlet and triplet excited states may (5) *covalently bridge* to the vinyl group, as in eq 1. Such bonding between two π systems

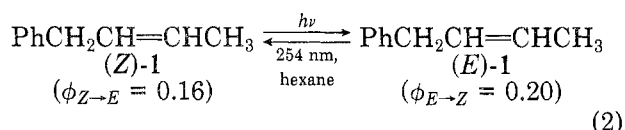


flanking a central sp^3 carbon initiates the photochemical "di- π -methane" rearrangement to vinylcyclopropanes;⁶ partial "di- π -methane" bonding may be the source of the decay described in (4) above.

1-Phenyl-2-butene (1).⁷ Our interest in bichromophores originated with this molecule.^{7a} As new tools have become available over the succeeding years, additional aspects of this compound's photophysics have continuously been uncovered.^{7b-e} It serves as an excellent example for the type of questions we and others have been asking and the methods which have been used to obtain answers. The fundamental observation is that irradiation of 1 in hexane solution using 254-nm light efficiently effects *E/Z* isomerization about the double bond (eq 2). The sensitization must be intramolecular, since added 2-hexene neither quenches the reaction nor is itself isomerized. Piperylene, an excellent triplet quencher ($E_T \sim 59$ kcal/mol), is also not

(6) S. S. Hixon, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973). A zwitterionic intermediate has also been suggested, and there is good evidence for a concerted mechanism in many cases.

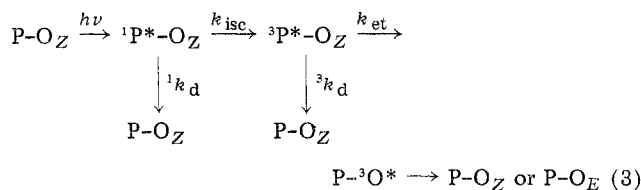
(7) (a) H. Morrison, *J. Am. Chem. Soc.*, **87**, 932 (1965); (b) H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968); (c) H. Morrison, J. Pajak, and R. Peiffer, *ibid.*, **93**, 3973 (1971); (d) H. Morrison, T. Nyland, and F. Palensky, *J. Chem. Soc., Chem. Commun.*, **4** (1976); (e) D. Giachero, unpublished data.



isomerized.⁸ Relevant absorption, photoelectron,⁹ fluorescence, and phosphorescence spectral data are summarized in Table I, together with data for such monochromophoric analogues as toluene (2) and 1-phenylbutane (3).

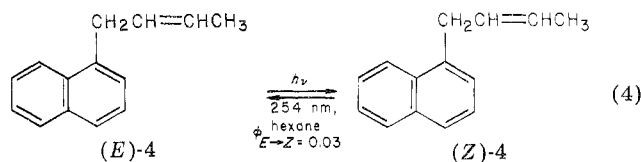
The picture which evolves from these data is that of a phenyl group which has its ground and lowest lying singlet states virtually unperturbed, despite the two functional groups lying close in space and being insulated by only a single methylene unit. This is clearly not the case for the triplet, the predominant involvement of which was confirmed by use of the "heavy atom effect", i.e., the ability of atoms of high atomic number to increase the rate and efficiency of intersystem crossing.⁵ Xenon, being inert and transparent, is particularly useful in this regard, and 1-phenyl-2-butene isomerization is enhanced by 43% with xenon, relative to argon.¹⁰

One is thereby led to a mechanism in which *the double bond is activated by intramolecular triplet energy transfer* (cf. eq 3, in which P and O represent the non-



conjugated phenyl and olefin moieties). Note that the energy-transfer step may also be viewed as T_2 (i.e., aryl) to T_1 (i.e., vinyl) radiationless decay. In fact, chemistry from T_2 appears to have been observed upon irradiation of 1 in the gas phase¹² where, upon photolysis at low pressure, a di- π -methane rearrangement competes with *E/Z* isomerization. (The rearrangement disappears at higher pressures and is not observed in solution.) *The rate constant for internal energy transfer (k_{et}) of 1 in solution can be estimated as $\geq 5 \times 10^9 \text{ s}^{-1}$, using the minimal amount of (diffusion-controlled)⁵ external diene isomerization observed on prolonged irradiation with piperylene.*

A plausible alternative mechanism for isomerization of 1, involving reversible di- π -methane bonding, has recently been ruled out by observing that 1-naphthyl-2-butene (4) isomerizes much less efficiently (eq 4).¹³



(8) Piperylene does quench the photoisomerization of 1 but by interception of the aryl singlet rather than the triplet. This is indicated by a comparable rate of quenching of the fluorescence from 1. The mechanism involves singlet exciplex formation.⁵

(9) E. Heilbronner, C. Batich, and H. Morrison, unpublished data. See also D. F. Eaton and T. G. Traylor, *J. Am. Chem. Soc.*, **96**, 7109 (1974), for data for allylbenzene.

(10) Xenon enhancement is unambiguous evidence for predominant triplet involvement so long as $\phi_{\text{isc}} \geq 0.50$,¹¹ which is in fact the case (see below).

(11) See ref 1a and references therein.

(12) M. Comtet, *J. Am. Chem. Soc.*, **92**, 5308 (1970).

The efficiency of di- π -methane bonding in 4 should be comparable to that for 1,¹⁴ whereas triplet-energy transfer from the lowest aryl triplet is no longer feasible (i.e., naphthyl $E_T \sim 61$ kcal/mol;¹⁵ butene $E_T \sim 78$ kcal/mol).¹⁶ The residual isomerization that is observed for 4 may well be due to di- π -methane bonding or conceivably naphthyl T_2 sensitization.¹⁷

Note that radiationless decay from the phenyl triplet (3k_d) is incorporated into eq 3. That there is such decay, sufficiently rapid to compete with internal energy transfer in aryl olefins, has become apparent only recently with the advent of xenon perturbation techniques.^{1a,18} As initially developed, the method was utilized for determining a substrate's ϕ_{isc} . Several reaction tubes are loaded with a solution of substrate and a "probe" compound to which triplet energy may be readily transferred. (Simple alkenes are frequently employed because the amount of alkene triplet formed is revealed by the degree of *E/Z* isomerization, which is in turn readily assayed by VPC.) Xenon (or another heavy-atom reagent) is then added to each tube, with progressively increasing amounts across the series. The fluorescence of the substrate is measured and the tubes are then photolyzed. One observes that as a tube's xenon content is increased, its substrate fluorescence is diminished and its probe triplet product formation is enhanced. The relationship is that given in eq 5,

$$[(F_0/F) - 1] = \phi_{isc}[(F_0/F)(P/P_0) - 1] \quad (5)$$

where F , P , F_0 , and P_0 are fluorescence and product formation, with and without xenon.¹⁹ There are two significant extensions of the method: (1) the "probe" may be built into the molecule (i.e., the olefin in 1) and (2) the equation is readily modified to accommodate a singlet component to the probe reaction product (eq 6).¹⁸

$$[(F_0/F) - 1] = \phi_{isc} \frac{\phi_P}{^3\phi_P} [(F_0/F)(P/P_0) - 1] \quad (6)$$

In this expression, ϕ_P and $^3\phi_P$ are the total and the triplet portions of the reaction, respectively, and $^3\phi_P = \phi_{isc}\phi_{RT}$, with ϕ_{RT} being the "intrinsic triplet reactivity" (the fraction of triplets which go on to product). The slope of a plot of eq 6 thus provides ϕ_{RT} without the necessity of measuring ϕ_{isc} (eq 7). Such a plot for

$$\text{slope} = \phi_{isc}\phi_P/{}^3\phi_P = \phi_P/\phi_{RT} \quad (7)$$

1-phenyl-2-butene yields a slope of 0.51^{7e} (exactly equal to the ϕ_{isc} of 0.51 for toluene,²⁰ as one would expect if the reaction is 100% triplet derived). With $\phi_P = \phi_{E \rightarrow Z} + \phi_{Z \rightarrow E} = 0.36$, ϕ_{RT} may be calculated as 0.71, which is

(13) D. Shade, M.S. Thesis, Purdue University, 1978.

(14) H. E. Zimmerman and M. L. Viriot-Villaume, *J. Am. Chem. Soc.*, **95**, 1274 (1973).

(15) S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973.

(16) G. P. Semeluk and R. D. S. Stevens, *Can. J. Chem.*, **49**, 2452 (1971); W. R. Flicker, Ph.D. Thesis, California Institute of Technology, 1976.

(17) C. C. Ladwig and R. S. H. Liu, *J. Am. Chem. Soc.*, **96**, 6210 (1974); **98**, 8093 (1976).

(18) F. Palensky, Ph.D. Thesis, Purdue University, 1977.

(19) R. H. Fleming, F. H. Quina, and G. S. Hammond, *J. Am. Chem. Soc.*, **96**, 7738 (1974).

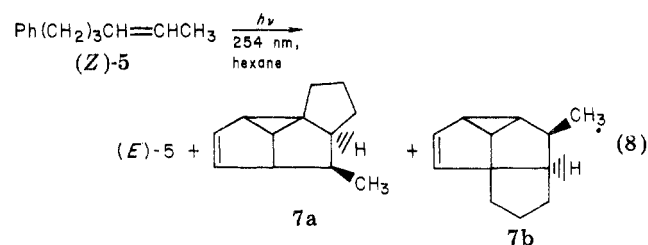
(20) F. A. Carroll and F. H. Quina, *J. Am. Chem. Soc.*, **98**, 1 (1976), and references therein.

Table II
Summary of Spectral Data for (*Z*)-6-Phenyl-2-hexene (5)
Relative to 1-Phenylhexane (6)

type of spectroscopy	principal observations
absorption	$^1B_{2u}$ transition virtually superimposable on that of 6
photoelectron fluorescence	5: 8.72, 9.24 eV; 6: 8.64, 9.25 eV emission superimposable on that of 6 but intensity and lifetime greatly reduced; 5, $\phi_f = 0.006$, $^1\tau = 1.0$ ns; 6, $\phi_f = 0.13$, $^1\tau = 35.0$ ns; fluorescence returns to "normal" intensity at 77 K in EtOH
phosphorescence	none observable from 5

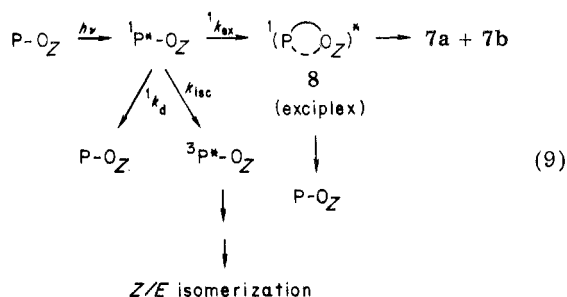
to say, 29% of the 1-phenyl-2-butene triplets is unaccounted for. Since there is no other reaction in solution, these triplets must decay without isomerization about the double bond. The rate of this decay may be calculated from $^3\phi_d = ^3k_d/(^3k_d + k_{et})$, so that with $^3\phi_d = 0.29$ and $k_{et} \geq 5 \times 10^9$ s⁻¹, $^3k_d \geq 2 \times 10^9$ s⁻¹. Such rapid radiationless decay is clearly not present in the longer-lived aryl alkane triplets, but is observed in other non-conjugated aryl olefins (see below).²¹

6-Phenyl-2-hexene (5).^{7e,22} A study of this molecule has provided evidence for a third mode of aryl-olefin interaction, i.e., intramolecular singlet exciplex formation. The photochemistry of (*Z*)-5 is shown in eq 8; the



E isomer reacts in analogous fashion, but the site of addition to the ring is altered. The intramolecular cycloaddition is quite efficient ($\phi_7 = 0.26$), but $\phi_{Z \rightarrow E}$ is only 0.01. Note that the 1,3-cycloaddition proceeds with retention of the cisoid relationship in 7a and 7b. Again, spectroscopy provides the requisite mechanistic clues for this reaction (Table II).

It is evident that the aryl excited singlet state is rapidly and efficiently intercepted by the olefin, though there is no spectral evidence for appreciable ground-state interaction. We thus propose a mechanism (eq 9) involving a "postexcitation" conformational reorien-



tation leading to an intramolecular exciplex (8). This exciplex may then decay radiationlessly or close to cy-

(21) It is tempting to speculate that the decay may involve incomplete di- π -methane-like bonding from the aryl (i.e., molecular T_2) state.

(22) (a) H. Morrison and W. Ferree, Jr., *J. Chem. Soc., Chem. Commun.*, 268 (1969); (b) W. Ferree, Jr., J. Grutzner, and H. Morrison, *J. Am. Chem. Soc.*, **93**, 5502 (1971).

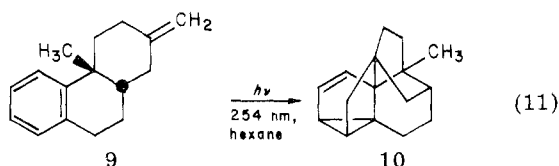
cladduct(s), a mechanistic sequence subsequently confirmed by numerous studies of intermolecular aryl-olefin cycloadditions.²³

The rate of complexation ($^1k_{ex}$) is readily calculated using $^1\tau$ for **5** (eq 10), if one assumes irreversible com-

$$^1\tau_5 = 1 / (^1k_d + k_{isc} + ^1k_{ex}) \quad (10)$$

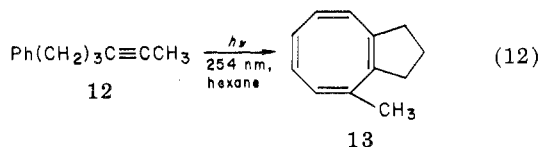
plexation and competitive photophysical rates (1k_d , k_{isc}) identical with those of **6** (i.e., $1/^1\tau_6$). The value obtained is $^1k_{ex} = 1 \times 10^9 \text{ s}^{-1}$. If a coplanar arrangement of olefin and benzene ring is required for exciplex formation, the trimethylene chain must reorient from its anti,anti conformation to a folded gauche,gauche form. Assuming the rate of complexation is determined by this reorientation (i.e., is "rotationally controlled"), $^1k_{ex}$ corresponds to the rate of conformational reorganization in a trimethylene chain ($A(CH_2)_3B$), and, in fact, identical values for this rate have been obtained using charge transfer in photoexcited anthracene- $(CH_2)_3-N,N$ -dimethylaniline²⁴ and intramolecular excited complex ("excimer")⁵ formation in 1,3-diphenylpropane.²⁵ The separation of two groups by three methylenes is particularly^{25a} (though not uniquely)² well suited for rotational interaction (" $n = 3$ rule").²⁶

An interesting reaction analogous to that in eq 8 is provided by the *cis*-decalin **9**; it too undergoes intramolecular, singlet-derived, 1,3-cycloaddition (eq 11; $\phi_{10} =$



0.046).^{27,28} The requisite conformational isomerization is now half-chair/chair to half-chair/boat. $^1k_{ex} = 4.5 \times 10^6 \text{ s}^{-1}$, corresponding to $\Delta G_{298K}^\ddagger = 8.3 \text{ kcal/mole}$; this is in excellent agreement with the chair to boat data for methylenecyclohexane ($\Delta G_{160-197K}^\ddagger = 8.4 \text{ kcal/mol}$).²⁹

The ability of the olefin group in **5** to internally quench aryl fluorescence is mimicked but muted when the olefin is replaced by an acetylene group (as in **12** where fluorescence is reduced by 15%). The (1,2) intramolecular cycloaddition (eq 12) is likewise much less



(23) For a review, see D. Bryce-Smith and A. Gilbert, *Tetrahedron*, **33**, 2459 (1977).

(24) T. J. Chuang, R. J. Cox, and K. B. Eisenthal, *J. Am. Chem. Soc.*, **96**, 6828 (1974).

(25) (a) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1963); W. Klopffer and W. Liptay, *Z. Naturforsch. A* **25**, 1091 (1970).

(26) There have been numerous photochemical and photophysical studies of $A(CH_2)_nB$ or similar systems. Representative examples include J. H. Borkent, A. W. J. DeJong, J. W. Verhoeven, and Th. J. De Boer, *Chem. Phys. Lett.*, **57**, 530 (1978); N. Mataga, M. Migita, and T. Nishimura, *J. Mol. Struct.*, **47**, 199 (1978); M. Goldenberg, J. Emert, and H. Morawetz, *J. Am. Chem. Soc.*, **100**, 7171 (1978); P. J. Wagner and B. J. Scheve, *ibid.*, **101**, 378 (1979); A. Gilbert and G. N. Taylor, *J. Chem. Soc., Chem. Commun.*, 229 (1979). See also M. A. Winnik, *Acc. Chem. Res.*, **10**, 173 (1977).

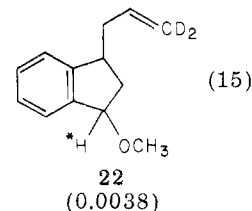
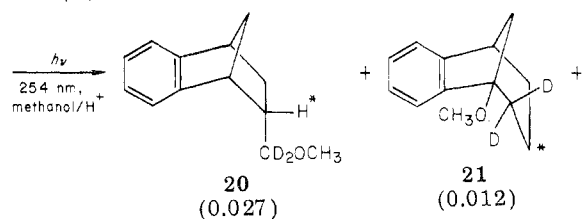
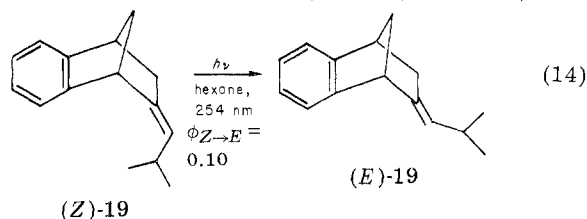
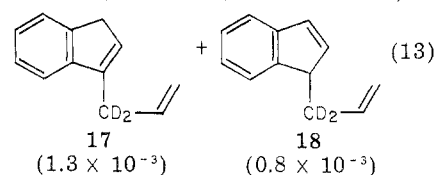
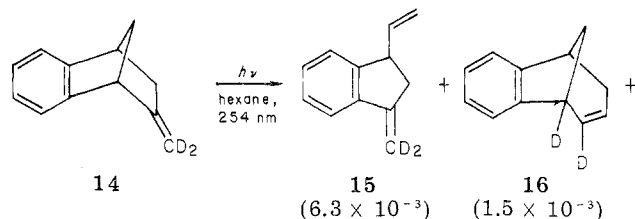
(27) M. Palmer, Ph.D. Thesis, Purdue University, 1978. M. Palmer and H. Morrison, submitted for publication.

(28) The *trans*-fused isomer of **9** (11) is photoinert; remarkably, though the aryl and olefin groups in **11** are separated by ca. 4.4 Å, there is no detectable phosphorescence from this compound (in fact, we have yet to observe phosphorescence from a nonconjugated aryl olefin!).

(29) J. T. Gerig and R. A. Rimerman, *J. Am. Chem. Soc.*, **92**, 1219 (1970).

efficient ($\phi_{13} = 3.3 \times 10^{-3}$).³⁰ However, the ability of **12** to (triplet) sensitize 2-heptene *E/Z* isomerization without affecting production formation confirms the role of the singlet state, and a mechanism analogous to eq 9 is proposed.³⁰

2-Methylenebenzonorbornene (**14**).^{1a,7d,31} This compound exemplifies our use of rigid molecules to study interactions in bifunctional molecules as a function of well-defined geometry. Its photochemistry has proven to be remarkably varied, with participation by both singlet and triplet excited states, and solvent polarity plays a major role in determining the course of reaction. The photochemistry is summarized in eq 13-15; quantum efficiencies are shown below the products.



In eq 15, hydrogens marked with an asterisk are replaced by deuterium when photolyses are conducted in CH_3OD .

Xenon perturbation studies indicate that all products *except* **20** are both singlet and triplet derived (cf. eq 6); these products are readily rationalized by invoking initial di- π -methane bonding (eq 16). The anti-Markovnikoff adduct, **20**, is unique in that its formation cannot be triplet (*p*-xylene) sensitized and is quenched appreciably by xenon. Other data pertinent to the formation

(30) W. Lippke, W. Ferree, Jr., and H. Morrison, *J. Am. Chem. Soc.*, **96**, 2134 (1974).

(31) (a) F. Scully, J. Grutzner, and H. Morrison, *J. Am. Chem. Soc.*, **95**, 5100 (1973); (b) H. Morrison and T. Nylund, *J. Chem. Soc., Chem. Commun.*, 785 (1976); (c) H. Morrison and T. Nylund, *ibid.*, 104 (1977); (d) T. Nylund and H. Morrison, *J. Am. Chem. Soc.*, **100**, 7364 (1978).

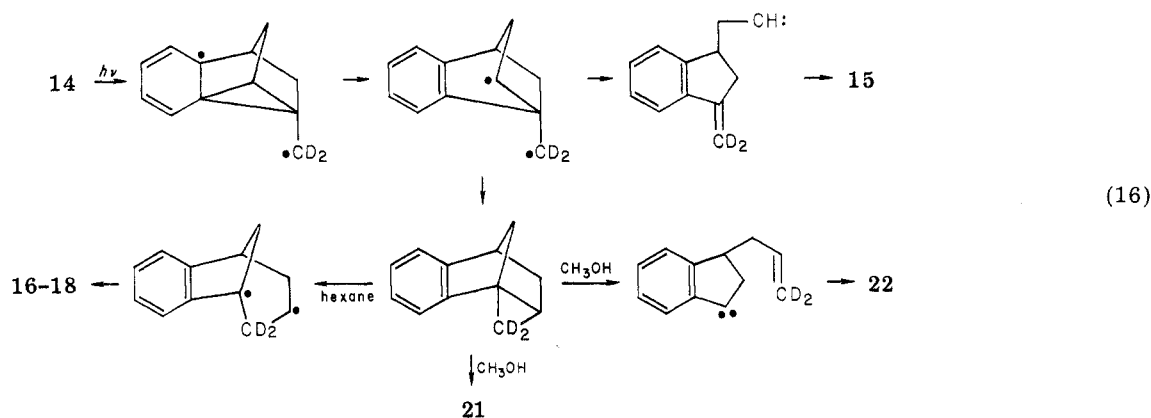
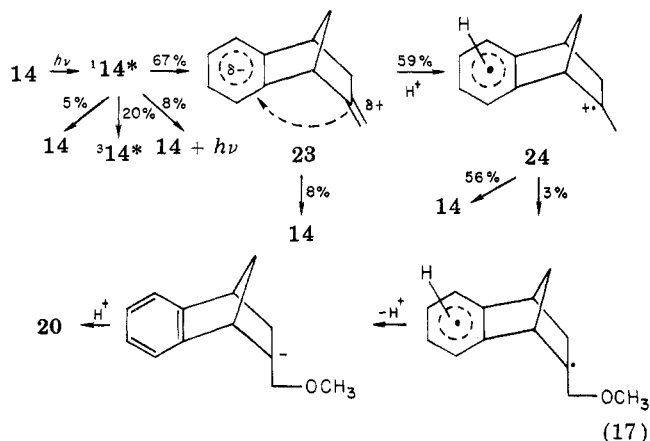


Table III
Summary of Spectral Data for
2-Methylenebenzonorbornene (14) Relative to
endo-2-Methylbenzonorbornene (28)

type of spectroscopy	principal observations
absorption	$^1B_{2u}$ transition red-shifted by ca. 2 nm relative to 28
photoelectron	14: 8.40, 8.90, 9.23 eV; benzonorbornene: ³⁵ 8.42, 8.93 eV; 2-methylenenorbornene: ³⁶ 9.04 eV
fluorescence	emission of 14 red-shifted by ca. 2 nm relative to 28; for 14 (hexane): $\phi_f = 0.08$, $^1\tau = 4.5$ ns; for 28: $\phi_f = 0.24$, $^1\tau = 13.5$ ns; a similar reduction in ϕ_f is observed at 77 K (by contrast with 5)
phosphorescence	none observable from 14

of 20 include (1) a linear dependence of ϕ^{-1} vs. $[H^+]^{-1}$ (indicating post excitation protonation), (2) the *lack* of an effect by acid on the fluorescence of 14 (indicating that protonation of the emissive S_1 state is *not* occurring), (3) the marked enhancement of addition when the electron affinity of the aromatic ring is increased by CF_3 substitution (ϕ increases by 60%) or the ionization potential of the olefin is lowered by methyl substitution (an 8-fold increase in ϕ), (4) the complete lack of addition or fluorescence quenching when a methoxy group is put on the aromatic ring.

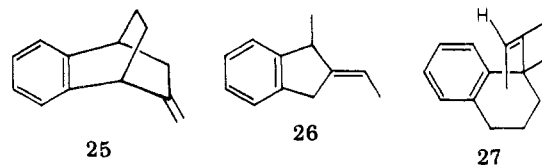
These data are best rationalized by the mechanism outlined in eq 17; the various numerical values were



obtained^{31d} by use of the fluorescence data for 14 (cf. Table III), $^1\tau$ and ϕ_{isc} of *endo*-2-methylbenzonorbornene (to provide k_{ic} and k_{isc}), and the slope of the ϕ^{-1} vs. $[H^+]^{-1}$ plot. Several features of the mechanism are noteworthy: (1) the requirement for several discrete

intermediates in addition to the emissive singlet ($^114^*$), (2) the appreciably reduced singlet lifetime and fluorescence yield of 14 due to rapid formation of the charge-transfer species, 23, (3) the "acid-assisted electron transfer" which creates the radical-cation 24.³² The singlet decay via 23 is to be distinguished from the sandwich-exciplex decay of 6-phenyl-2-hexene (5); the role of charge transfer in the latter case is yet to be probed but, significantly, 5 shows no such acid-catalyzed addition of methanol across the double bond.

Other molecules which show appreciably enhanced singlet radiationless decay but *no* solvent incorporation are 25³³ and 26.^{1a} The orthogonally arranged chromo-



phores in 27 give rise to very little aryl singlet perturbation.^{1a} Besides the *singlet* decay discussed above, 14 (and 26) display *triplet* radiationless decay analogous to that previously described for 1-phenyl-2-butene (1), i.e., triplet decay competitive with energy localization at the double bond and not involving olefin isomerization. Such decay accounts for 59 and 55% of the triplets of 14 and 26, respectively.

Finally, the relatively "clean" aryl spectral features of 1 and 5 are blurred somewhat in 14. Circular dichroism studies give evidence for a small perturbation of the $^1B_{2u}$ transition by the double bond.³⁴ Likewise, the photoelectron spectral data (Table III) are consistent with a small conjugative, through-space interaction ($C(Ph, \pi) \approx 0.10$ eV). Values for related molecules are given below, for purposes of comparison.³⁵⁻³⁷

(32) See M. Bellas, D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunkin, S. Krestonosich, C. Manning, and S. Wilson, *J. Chem. Soc., Perkin Trans. 1*, 2571 (1977), for a similar proposal.

(33) D. Neidigk and H. Morrison, *J. Chem. Soc., Chem. Commun.*, 600 (1978); D. Neidigk, M.S. Thesis, Purdue University, 1978.

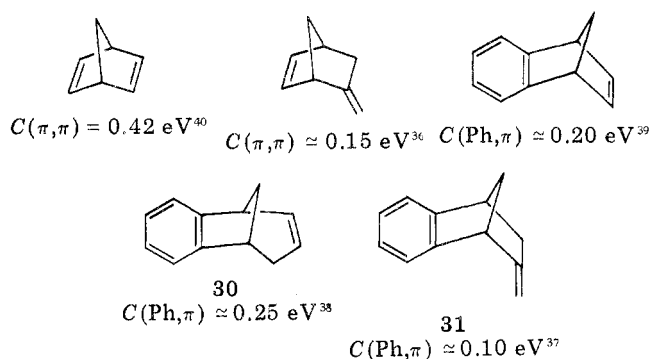
(34) D. J. Sandman and K. Mislow, *J. Am. Chem. Soc.*, **91**, 645 (1969); W. H. Inskip, D. W. Miles, and H. Eyring, *ibid.*, **92**, 3866 (1970).

(35) I. Morishima, K. Yoshikawa, M. Hoshimoto, and K. Bekki, *J. Am. Chem. Soc.*, **97**, 4283 (1975).

(36) P. Asmus and M. Klessinger, *Tetrahedron*, **30**, 2477 (1974).

(37) Calculations of "conjugative" interactions are highly approximate, due to the assumptions involved in estimating the associated "inductive" effects (there is an excellent recent discussion by Houk et al.).³⁸ The value presented here for 14 is by the method described in ref 38, using inductive effect values estimated by Haselbach and Rossi,³⁹ modified as was done for compound 30.³⁸

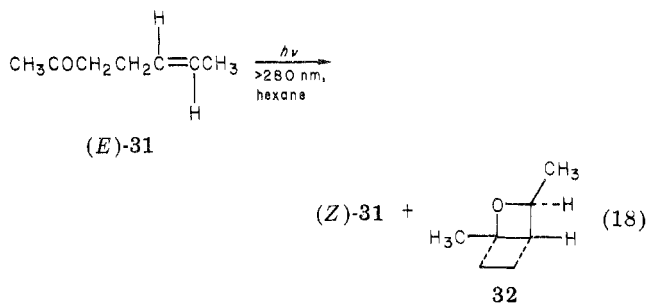
(38) L. N. Domelsmith, P. D. Mollere, K. N. Houk, R. C. Hahn, and R. P. Johnson, *J. Am. Chem. Soc.*, **100**, 2959 (1978).



Nonconjugated Keto Olefins

This family of bichromophores rivals the aryl olefins in the amount of effort devoted to their study. Though the bulk of recent research has involved β,γ -unsaturated ketones,⁴¹ our own studies have focused on two γ,δ -unsaturated ketones: 5-hepten-2-one and 1-phenyl-4-hexen-1-one. When examined in detail, the former reveals unexpected similarities to 6-phenyl-2-hexene in its photochemical and photophysical properties, while the latter further illustrates the rapidity of intramolecular singlet and triplet interactions.

5-Hepten-2-one (31).^{7a,42} Irradiation of (*E*)-31 in hexane results in *E* → *Z* isomerization ($\phi = 0.02$) as well as oxetane formation (32, $\phi = 0.016$) (eq 18). The *Z*



isomer likewise isomerizes ($\phi = 0.029$), but gives no oxetane. Quenching experiments on (*E*)-31 using piperylene demonstrate that the cycloadduct is not quenched (i.e., it is singlet derived), while *E/Z* isomerization is quenched, albeit inefficiently (k_q for the triplet portion = 0.9 M^{-1}) and incompletely (the unquenchable (i.e., singlet) fraction is ca. 67%). The k_q calculated from the quenching slope, assuming k_q is diffusion controlled ($1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$),⁴³ is $7 \times 10^{-11} \text{ s}$. This very short lifetime is reflected in the inability of piperylene to intercept (*E*)-31 triplets at a concentration (0.04 M diene) sufficient to completely trap those of 2-hexanone. The triplet lifetime for 31 is therefore a consequence of a new decay mode for the carbonyl triplet (i.e., intramolecular energy transfer),⁴⁴ the rate constant for which is $\sim 1.4 \times 10^{10} \text{ s}^{-1}$ (recall $k_{\text{et}} \geq 5 \times 10^9 \text{ s}^{-1}$ in 1-phenyl-2-butene).

(39) E. Haselbach and M. Rossi, *Helv. Chim. Acta*, **59**, 278 (1976). The value of $C(\text{Ph},\pi)$ given here is the empirical number after correcting for inductive effects.

(40) E. Heilbronner, *Isr. J. Chem.*, **10**, 143 (1972).

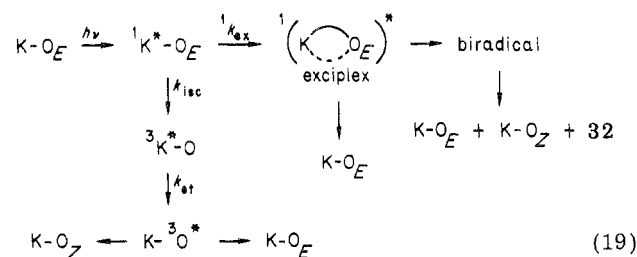
(41) K. N. Houk, *Chem. Rev.*, **76**, 1 (1976).

(42) S. R. Kurowsky and H. Morrison, *J. Am. Chem. Soc.*, **94**, 507 (1972).

(43) P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968).

(44) Assuming no extensive, undetected triplet radiationless decay as in the aryl olefins. Unfortunately, ${}^1n,\pi^*$'s are not susceptible to heavy-atom perturbation.

Such rapid internal triplet energy transfer should have produced considerably more olefin isomerization than is observed⁴⁴ were ϕ_{isc} for the ketone "normal". This hint that ${}^1\tau$ (and therefore ϕ_{isc}) has also been considerably diminished is confirmed by the complete absence of fluorescence from 31. Thus, a new photophysical act dominates the carbonyl singlet state; it is attributed to intramolecular exciplex formation, quite analogous to that observed for 6-phenyl-2-hexene (5). Although the exciplex primarily decays unproductively back to (*E*)-31, there is some chemical bonding to a biradical which may then close to 32 or fall apart to give (*E*)- and (*Z*)-31. If one assumes $k_{\text{isc}} \sim 4 \times 10^8 \text{ s}^{-1}$ ⁴⁵ and $\phi_{\text{isc}} \geq 0.02$ (an efficiency sufficient to produce the observed level of triplet derived *E/Z* isomerization),⁴⁴ the rate of exciplex formation is ${}^1k_{\text{ex}} \leq 2 \times 10^{10} \text{ s}^{-1}$. This may be compared to ${}^1k_{\text{ex}} = 1 \times 10^9 \text{ s}^{-1}$ for 6-phenyl-2-hexene, in which the two moieties are separated by an additional methylene unit. The mechanism is outlined in eq 19 (compare eq 9).



The same picture emerges from studies of acylbornenes,^{46,47} and the basic elements of the mechanism in eq 19 have been confirmed using β -oxa- γ,δ -enones.⁴⁸ Similar interactions have been observed with δ,ϵ -unsaturated aldehydes,⁴⁹ and there is evidence that an aromatic ring can play a role similar to that of the double bond, in nonconjugated aryl ketones.^{50,51}

1-Phenyl-4-hexen-1-one (35).⁵² The rapidity of intramolecular keto/olefin singlet exciplex formation is reflected in the virtual elimination of Norrish type II reactivity from the carbonyl singlet states of 33⁴² and 34.⁴⁶ Another indication of the efficacy of such complexation is provided by 35, where interaction would have to compete with the 10–100-fold increase in k_{isc} associated with aryl ketones.⁵³ Nevertheless, singlet

(45) N. C. Yang, E. D. Feit, M. H. Hui, N. J. Turro, and J. C. Dalton, *J. Am. Chem. Soc.*, **92**, 6974 (1970).

(46) (a) R. R. Sauers and T. R. Henderson, *J. Org. Chem.*, **39**, 1850 (1974); (b) R. R. Sauers, A. D. Rouseau, and B. Byrne, *J. Am. Chem. Soc.*, **97**, 4947 (1975).

(47) See also B. Furth, G. Daccord, and J. Kossanyi, *Tetrahedron Lett.*, 4259 (1975).

(48) J. C. Dalton and S. J. Tremont, *J. Am. Chem. Soc.*, **97**, 6916 (1975).

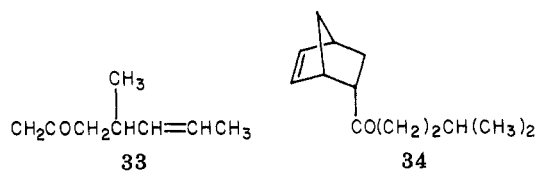
(49) B. Guiard, B. Furth, and J. Kossanyi, *Bull. Soc. Chim. Fr.* (2), 1552 (1976), and previous papers.

(50) R. R. Sauers and A. M. DePaolis, *J. Org. Chem.*, **38**, 639 (1973); G. L. B. Carlson, F. H. Quina, B. M. Zarnegar, and D. G. Whitten, *J. Am. Chem. Soc.*, **97**, 346 (1975), and references therein; J. Moron and G. Roussi, *J. Org. Chem.*, **43**, 4215 (1978). The photophysics and photochemistry of these molecules appear to be a more complex function of interchromophoric interactions. For example, there is a surprising lack of reactivity in the (n,π^* ?) triplet.

(51) For a summary of intermolecular carbonyl/olefin interactions in the singlet state, see N. C. Yang, M. H. Hui, D. M. Shold, N. J. Turro, R. R. Hautala, K. Darves, and J. C. Dalton, *J. Am. Chem. Soc.*, **99**, 3023 (1977).

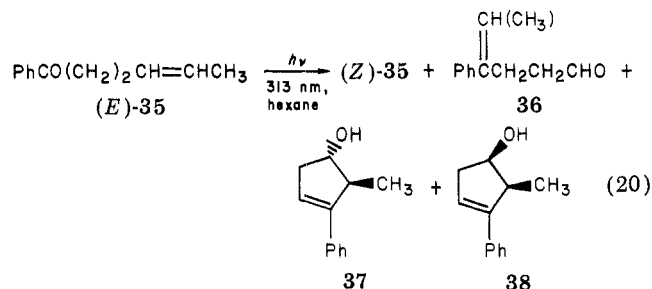
(52) H. Morrison, V. Tisdale, P. J. Wagner, and K.-C. Liu, *J. Am. Chem. Soc.*, **97**, 7189 (1975); V. Tisdale, Ph.D. Thesis, Purdue University, 1976.

(53) R. M. Hochstrasser, H. Lutz, and G. W. Scott, *Chem. Phys. Lett.*, **24**, 162 (1974), and references therein.



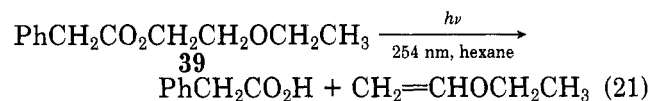
complexation remains competitive and reduces ϕ_{isc} (determined by energy transfer to piperylene ("triplet counting")⁵⁵) to 0.61 ± 0.05 . If one assumes $k_{\text{isc}} \leq 4 \times 10^{10} \text{ s}^{-1}$, $^1k_{\text{ex}}$ is $\leq 2.6 \times 10^{10} \text{ s}^{-1}$ (compare for 5-hepten-2-one, $^1k_{\text{ex}} \leq 2 \times 10^{10} \text{ s}^{-1}$).

A small amount of singlet *E/Z* isomerization results from complexation, but the observed photochemistry (eq 20) is predominantly triplet derived (36–38 result

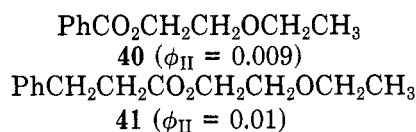


from an intermediate oxetane). The triplet products presumably arise via a triplet exciplex,⁵⁴ the rate for formation of which ($^3k_{\text{ex}}$) is $\sim 0.5\text{--}1.0 \times 10^{10} \text{ s}^{-1}$, as determined by triplet counting and quenching plots.⁵⁵

Nonconjugated Aryl Esters. Photolysis of 2-Ethoxyethyl Phenylacetate (39).⁵⁶ The facile Norrish type II fragmentation of 39 (eq 21), using 254-nm light,



exemplifies yet another mode of functional group interaction. The efficiency ($\phi = 0.10$) is actually 10-fold higher than that for both the conjugated benzoate (40) and the propanoate (41). There is ample evidence that



the reaction derives from an excited singlet state. Thus, piperylene quenches the reaction and fluorescence

with comparable efficiency, even though there is additional quenching of triplets, as evidenced by *E/Z* isomerization of the diene (which measurement yields, after correction for singlet quenching, a ϕ_{isc} for 39 of 0.40). Also, the fragmentation of *threo*- and *erythro*-1,2-dimethylbutyl phenylacetate is >90% stereoselective, as one would anticipate for an intermediate short-lived, singlet diradical.^{57,58}

The question then is how the normally transparent ester function is excited by 254-nm light.⁵⁹ Since ethyl acetate does not quench the reaction, transmission of excitation is strictly intramolecular. A rapid singlet-energy transfer between the two functionalities is attractive, but suffers from the lack of any indication that S_1 for the ester would lie below S_1 for the phenyl group.⁵⁹ The alternative is that the two functional groups are strongly coupled and form a "super chromophore" in which excitation is "delocalized" over both moieties. There is support for this picture in the absorption spectrum, which shows the largest perturbation of all the compounds discussed in this Account. The minimum preceding end absorption is displaced ca. 17 nm to the red relative to toluene, and the $^1B_{2u}$ band is appreciably reduced in intensity. Both features are less pronounced (though still apparent) in the much less reactive propanoate (41). The fluorescence and phosphorescence of 39 are also reduced (by 80 and 40%, respectively) relative to toluene, though the band positions remain characteristic of an alkylbenzene. Evidence which would confirm one of these mechanisms (or an alternative) is still lacking.

Concluding Remarks

The substrates reviewed above serve to illustrate the difficulties facing a photochemist who attempts to predict the excited-state properties of multifunctional molecules using *only* a background of monochromophore chemistry. Conversely, the diversity of photo-physical and photochemical phenomena evident in even the small number of molecules discussed confirms that multichromophoric compounds will provide a fruitful area of investigation for photochemists, spectroscopists, and theoreticians for some time to come.

I wish to acknowledge the efforts of all my students at Purdue, who have worked so hard to bring these studies to fruition. The financial assistance of the National Science Foundation, U.S. Army Research Office, Purdue Research Foundation, Standard Oil of Ohio, and Phillips Petroleum Company is also gratefully acknowledged. This article was written while I enjoyed the gracious hospitality of the Dyson Perrins Laboratory of Oxford University.

(57) J. E. Gano, *Mol. Photochem.*, **3**, 79 (1971).

(58) There has been some debate as to whether *trans* or *cis* elimination, in appropriately configured cyclohexanes, is preferred; cf. G. Eadon, E. Bacon, and P. Gold, *J. Org. Chem.*, **41**, 171 (1976), and references therein.

(59) For a recent review of the spectroscopy and photochemistry of esters, see J. D. Coyle, *Chem. Rev.*, **78**, 97 (1978).

(54) I. Kochevar and P. J. Wagner, *J. Am. Chem. Soc.*, **94**, 3859 (1972); R. A. Caldwell, G. W. Sovocool, and R. P. Gajewski, *ibid.*, **95**, 2549 (1973).

(55) See ref 46b for a study of *endo*-5-benzoylnorbornene. See also D. Cowan and A. A. Baum, *J. Am. Chem. Soc.*, **93**, 1153 (1971), and P. J. Wagner, T. Jellinek, and A. E. Kempainen, *ibid.*, **94**, 7512 (1972), for reports on benzoylstyrenes and benzoylamines, respectively.

(56) H. Morrison, R. Brainard, and D. Richardson, *J. Chem. Soc., Chem. Commun.*, 1653 (1968); R. Brainard and H. Morrison, *J. Am. Chem. Soc.*, **93**, 2685 (1971).