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PHOTOCHEMISTRY OF ACYLPHENYL OLEFINIC ESTERS

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Fenton Ransom Heirtzler

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Peter Wagner
Major professor

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PHOTOCHEMISTRY OF ACYLPHENYL OLEFINIC ESTERS

By

Fenton Ransom Heirtzler

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ABSTRACT

PHOTOCHEMISTRY OF ACYLPHENYL OLEFINIC ESTERS

by

Fenton Ransom Heirtzler

The triplet lifetimes and quantum yields for Type II cleavage of 4'-valeryl alkenyl benzoates and 4'-butyrylphenyl alkenoates were determined by Stern-Volmer kinetics relative to those of 4'-valeryl methyl benzoate and 4'-butyrylphenyl acetate in benzene and 4:1 - methanol:benzene, respectively. Intramolecular charge transfer quenching by the tethered olefin of the alkyl phenone π,π^* triplet state with rate constant, $k_{CT} = 1.3 \times 10^7 \pm 3 \times 10^6\ s^{-1}$ was shown to contribute significantly to triplet decay processes of 4'-butyrylphenyl 3-butenoate. The absence of similar phenomena from the 4'-valeryl -allyl-, -3-butenyl- and -3-methyl-2-butenyl benzoate and 4'-butyrylphenyl 4-pentenoate esters was attributed to poor overlap geometry of the photosubstrate -olefines and -aromatic rings. Preparative irradiations of 4'-acetyl -allyl- and -3-butenyl- benzoate, 4'-acetylphenyl 3-butenoate and 5'-acetyl-2'-methoxy -allyl- and -3-butenyl benzoate gave only unidentified materials from polymerisation and photoreduction.

The $^3\pi,\pi^*$ configuration of 4'-valerylphenyl acetate in benzene was estimated to be preferred over the $^3\pi,\pi^*$ one by ca. 0.6 kcal/mol.

No photo-Fries type products were detected in the photolyses of the acetate esters.

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The author wishes to thank Professor Peter J. Wagner for seeing him through this degree. His concern for the author's future education is deeply appreciated.

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To my Family

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INTRODUCTION

I. FUNDAMENTALS

A. Formation of the Triplet State

The absorption of a suitable photon of light by a molecule promotes an electron from a π- or nonbonding- orbital to an antibonding orbital. The electronically excited molecule can exist in either the singlet state, where the promoted electron is spin-paired with that remaining in the original half-vacant orbital, or in the triplet state, where the electrons are spin-unpaired.

In the case of aromatic ketones, the upper vibrational level of a n,π^* singlet excited state is initally formed. This then rapidly deactivates to its lowest vibrational level[1] with a unimolecular rate constant of ca. 10^{12} s^{-1}, whereupon it predominantly undergoes intersystem crossing to either a n,π^* or π,π^* triplet state. Fluorescence is not a major phenomenon[2]. Because intersystem crossing is formally spin-forbidden, the magnitude of its rate constant, k_{isc} depends on the size of the singlet-triplet energy gap and the nature of the triplet state. For $^1n,\pi^* \rightarrow {}^3n,\pi^*$ and $^1n,\pi^* \rightarrow {}^3\pi,\pi^*$ transitions, $k_{isc} \approx 10^8$ and 10^{11} s^{-1}, respectively[3]. Vibrational relaxation again follows quickly. In the event of intersystem crossing to an upper electronically excited triplet state, population of the lower triplet occurs through internal conversion[4], k_{ic}<ca. 10^{10} s-1. The physical and chemical processes available to the triplet state after its final vibrational relaxation can now be considered.

B. Basic Photophysical Processes of Triplet Ketones

The triplet ketone can return to the ground state by the emission of light (phosphorescence) with a rate constant $k_p \approx 1 - 20\ s^{-1}$, at room temperature[5] or through a non-radiative process[1], characterised by k_{ir}<ca. 10^3. The slow, spin-forbidden nature of these processes gives triplets in general much greater lifetimes than their corresponding singlet excited states. In turn, this allows chemical reactions with rate constant k_R to compete with deactivation[5].

A modified Jablonski diagram neatly summarises the overall situation after excitation[6]. Here, the relative energies are displayed on the vertical axis, versus the excited states which they describe. Radiative transitions are described with straight arrows, while non-radiative ones are shown with wavy ones and chemical reactions are shown with darkened ones.

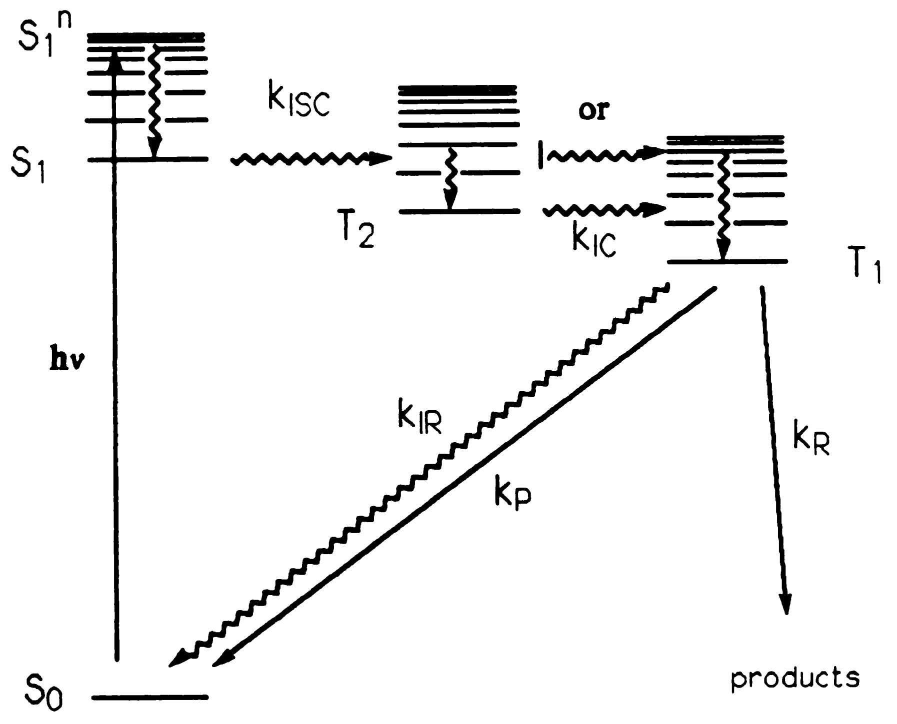


Figure 1. Jablonski Energy Diagram for Phenyl Ketones

II. TYPE II PHOTOREACTIVITY

A. *Mechanism*

A process common to the triplet state of many ketones posessing aliphatic hydrogen atom located γ to the carbonyl group is the Norrish Type II cleavage reaction. It was first noted in 1934 by Norrish and Appleyard[7], who detected the formation of acetone and propene during the gas phase photodecomposition of 2-hexanone.

It is now known to proceed through a n,π^* triplet state for phenyl ketones[8]. In the n,π^* triplet state, a carbonyl oxygen n-orbital electron is promoted to a π^* antibonding aromatic orbital. An electron deficient "hole" in the n-orbital electron density is thereby created. The carbonyl oxygen consequently reacts as an electrophilic species, typically abstracting hydrogen atoms from extra- and intra- molecular sources. In the former case, bimolecular photoreduction by solvents or additives containing labile hydrogen atoms to form benzpinacol-type products occurs[9]. In the latter instance, spatially accessible aliphatic hydrogen atoms elsewhere on the molecule, but often on the position γ to the ketone carbonyl of a C_3 or longer n-alkyl chain, are abstracted to form a hydroxy-1,4-biradical[10] with rate constant k_H. The intermediacy of this biradical has been indicated by spectroscopic[11] and trapping studies[10b]. It cleaves to the corresponding acetophenone enol and alkene according to k_{cl} and to a lesser extent cyclizes, k_{cy} to form a 1-phenylcyclobutanol derivative. Reverse hydrogen abstraction to reform the ground state starting ketone, k_{rev} also occurs[10c]. Experimentally, the overall rate constant for formation of cleavage products, k_{II} (vide infra) is usually measured.

The addition of regulated amounts of Lewis bases such as methanol, tert-butanol, p-dioxan or pyridine impedes reverse hydrogen transfer through hydrogen bonding to the hydroxyl group of the biradical[12]. The quantum efficiency of acetophenone and cyclobutanol formation are thus maximised at some certain concentration of Lewis base[12-14].

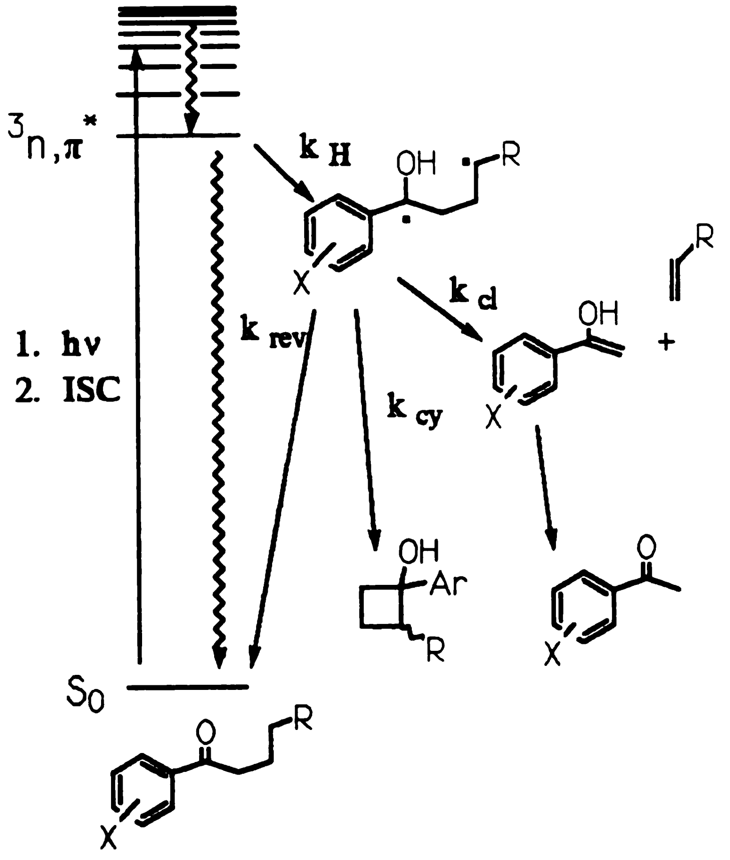


Figure 2. Type II Photoprocesses of Phenyl Alkyl Ketones

B. Aliphatic Substituents

The reactivity of the triplet ketone responds to resonance- and inductive- (de)stabilising groups adjacent to the alkyl radical site like that in simple radicals[15]. Good linear correlation is thus found in Hammett plots of relative rate constants of appropriately substituted butyrophenone and valerophenone derivatives versus σ inductive substituent constants[16]. Resonance electron -donating and -accepting substituents are also accounted for. The extensive amount of work carried out on the Type II process allows it to serve as a "clock" against which the rates of other processes can be compared[17,18].

C. Aromatic Substituents

The effect of ring substituents on the reactivity of triplet phenyl alkyl ketones is far more complicated, however. Relatively energetically proximate to the reactive n,π^* triplet is a π,π^* triplet state[4,19-22]. Its electronic configuration is a result of the promotion of an aromatic π electron to a carbonyl π^* orbital, increasing the carbonyl electron density. Consequently, Type II reactivity from phenyl alkyl ketones having π,π^* lowest triplet states is expected to be greatly decreased. Therefore, the effects of ring substituents on the electron deficient character of the carbonyl oxygen and the relative ordering of the energies of the two triplet states must both be considered[21]. The classical resonance forms which are thought to contribute significantly to each excited state are depicted in Figure 3.

Valerophenone derivatives ring-substituted with electron-withdrawing substituents, like o-, m- and p- F and CF_3, o-CN, m- and p-CO_2CH_3, o-OCF_3 and p-C(O)R (R= alkyl) show $k_{II\sim}$ 1×10^8 s^{-1} in benzene[21,23,24]. For electron-donating substituents[25,26] like m- and p- CH_3, o-, m- and p-OCH_3, p-SCH_3 and p-C_6H_5, $k_{II} \leq$ ca. 4×10^7 s^{-1}.

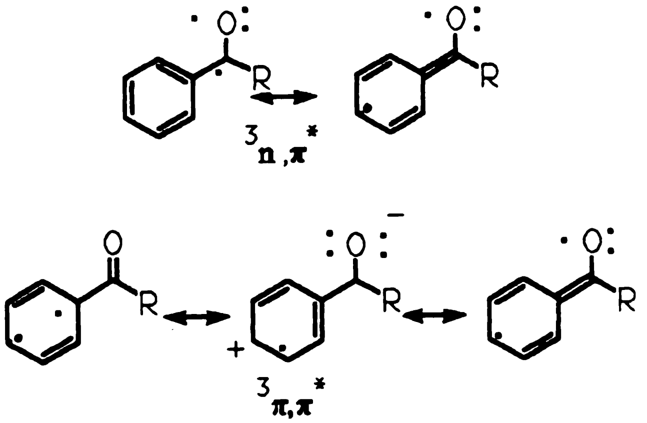


Figure 3. Resonance Contributors to Phenyl Ketone n,π^* and π,π^* Triplet States

Additionally, the o- and p-chlorovalerophenones show decreased values for k_{II}, while that of the meta isomer is closer to that of valerophenone itself[16,21].

However, attempted Hammett correlations of k_{II} values for these compounds relative to k_{II}^{o} for valerophenone versus σ parameters reveal regions of two different slopes- one for the meta- and para- inductively withdrawing groups and the other for resonance donating groups[21]. Rate constants for conjugating, electron withdrawing substituents like p-CO_2CH_3, p-CN, and m- and p- C(O)R deviate widely from either line[23].

According to classical precedent, this suggests the operation of at least two diffent mechanisms[27] for hydrogen abstraction. It is well established that inductively electron withdrawing substituents stabilise the n,π^* triplet state over the π,π^* triplet state by ca. 3.0 to 6.0 kcal/mole, relative to valerophenone, where this advantage is ca. 3.0 kcal/mole[21]. Introduction of donating substituents to the phenyl ring simultaneously destabilises the n,π^* triplet state and lowers the energy of the π,π^* triplet[24]. The latter is thought to stem from splitting of the π,π^* triplet state with the charge-transfer state and/or L_a spectroscopic states. The consequences of this effect range from rendering the triplet states of the methylvalerophenones approximately isoenergetic up to favouring the π,π^* triplet state of p-thiomethyoxyvalerophenone by ca. 10 kcal/mol over the n,π^* one[21].

The o- and p -Cl and p-carbomethoxyvalerophenones provide a mixed case, wherein the conjugative stabilization the π,π^* triplet state is partially offset by their inductive propensity toward hydrogen abstraction. This later notion is reinforced by the m -Cl, -CN and $-CO_2CH_3$ derivatives, where these electron withdrawing, non-conjugating substituents preclude any stabilisation through orbital mixing[23]; their lowest energy triplet is n,π^* in nature.

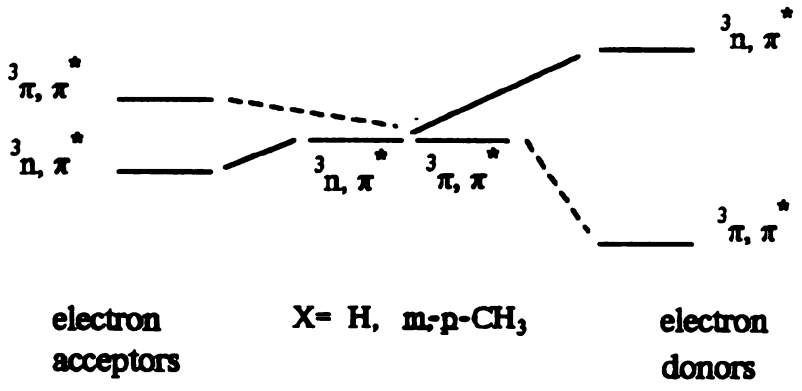


Figure 4. Influence of Aromatic Substituents on n,π^* and π,π^* Energy Levels

D. Triplet Equilibrium

A rationale to explain the Type II reactivity of π,π^* lowest triplet phenyl ketones is still necessary, however. Similarly, electron donor substituted acetophenones, benzophenones and acetylnaphthalenes (π,π^* lowest triplet) are moderately reactive to photoreduction[26].

It was postulated by Wagner 17 years ago that the reactivity of π,π^* lowest triplet phenyl ketones stemmed from a thermodynamic equilibrium between the unreactive π,π^* (T_1) and reactive n,π^* (T_2) states[21]. Thus, in theory the observed rate constant for hydrogen abstraction is proprotional to the partial rates from each triplet state. The equilibrium population of the states in turn depends on the energy difference $\Delta E = E_{n,\pi} - E_{\pi,\pi}$ between the two states according to a Boltzmann distribution function, Equation 1, where χ_i are the fractional populations of each state and R and T have their usual definitions. For $\Delta E \geq$ ca. 3 kcal/mol, or alternately assuming that the non-electrophillic nature of the π,π^* T_1 states must render their intrinsic, "pure" rate of hydrogen abstraction insignificant relative to that of T_2, Equation 2, where k_r^n is the rate constant for unadulterated n,π^* reactivity and k_r^{obsd}, the experimentally observed one, therefore describes the predicted rate dependence. Values of k_r^n can in turn be estimated, for example, by comparison to the photoreactivities of similarly substituted benzophenones[28] with known n,π^* lowest triplet states.[29]

$$\chi_{n,\pi}/\chi_{\pi,\pi} = e^{-\Delta E/RT} \tag{1}$$

$$k_r^{obsd} = \chi_{n,\pi} \cdot k_r^n \tag{2}$$

The validity of this theory was initally demonstrated by comparison of the Type II reactivities of series of anisoyl alkyl ketones ($T_1 = {}^3\pi,\pi^*$) and phenyl alkyl ketones ($T_1 = {}^3n,\pi^*$)[28]. Approximately the same relative change in photoreactivity as a function of substitution at the γ carbon was observed between each series.

The condition of exclusive n,π^* reactivity instead of, say, reactivity arising from the mixing of zero-order ${}^3n,\pi^*$ and ${}^3\pi,\pi$ states[26b] was also supported by measurements of activation energies for the photoreduction of definite $T_1 = {}^3n,\pi$ and ${}^3\pi,\pi$ acetophenones[30]. According to quantum mechanical- and kinetic- formulations, the detection of significant activation energies precluded that alternate theory from the current case, and the fact that the activation energies of the ${}^3\pi,\pi^*$ T_1 ketones were noteably higher than those of the ${}^3n,\pi^*$ ones implied that thermal equilibration to ${}^3n,\pi^*$ T_2 was a prerequisite for reactivity. This latter caveat was understandable because now, barring direct ${}^3\pi,\pi^*$ T_1 reactivity, the T_2-T_1 energy gap and the actual activation energy must both be surmounted for reaction to occur. Other, more recent cases where decreased reaction rates have been quantitatively related to the ${}^3n,\pi^*$ - ${}^3\pi,\pi^*$ energy gap include the photoreduction of acetophenones[28,30] and the α-photocleavage of aryl alkyl ketones[31]. It is also thought to account for the differences in excited state deactivation[32]- and yet other Type II photocleavage[33]-rates. The rate constant for formation of Type II cleavage products from p-carbomethoxyvalerophenone, 1.2 x 10^8 s^{-1} in benzene, has also been used to provide an estimate of the T_1 - T_2 energy gap in this chromophore, 0.3 kcal/mole. This agrees reasonably with the spectroscopically determined value[23]. Thus, the consequences of equilibrating ketone triplet states appear to be general.

E. Solvent Effects

Polar solvents also destabilise the n,π^*, triplet state of phenyl ketones relative to the ground state by hydrogen bonding to the carbonyl n-orbital electrons. The π,π^* triplet state is simultaneously stabilised through a related phenomenon[20a]. Decreased phosphorescence rates, indicative of the longer-lived π,π^* triplet state, have also been observed in polar media[20a]. Combined with the solvent effect on biradical revertibility, the net effect is mixed. Phenyl ketones with n,π^* lowest triplets show increased quantum yields with Lewis base concentration until a plateau near 1.0 is reached. However, in pure polar solvents[12-14,21],their k_{II} (an d k_H) values drop by ca. 50%. Those ketones having π,π^* lowest triplets show greatly decreased hydrogen abstraction rates, and their quantum yields are maximised at much lower Lewis base concentrations. A drastic decrease in quantum yields beyond this concentration then occurs[14].

III. QUENCHING

Quenching can be defined as the the deactivation of an excited state, mitigated by collision with another molecule, the quencher. Triplet aryl ketones are commonly quenched by energy- and/or charge-transfer processes.

A. Energy Transfer

Energy transfer (E.T.) occurs via a HOMO-HOMO/LUMO-LUMO (or vice versa) electron exchange mechanism. The long lifetimes of triplet species relative to singlet ones make this a common process[4]. It is most significant when the ketone triplet energy (for phenyl alkyl ketones, ca. 60 - 75 kcal/mol[21]) is greater than that of the quencher. It is characterised by experimental rate constants which are proportional to the size of the triplet energy difference until a maximum is reached. Geometrical constraints on the donor-acceptor orbital overlap and the efficiency of E. T. within the close-contact pair usually keep the rates below the diffusional limit[34] in less viscous solvents; $k_{diff} \approx 10^9\ \underline{M}^{-1}s^{-1}$. Conjugated butadienes (E_T= ca. 60 kcal/mol[35]) and molecular oxygen (E_T= 23 kcal/mol[35]) olefins are commonly encountered E. T. quenchers[4].

B. Charge Transfer

Charge transfer (C. T.) quenching occurs by a "half" exchange- for phenyl ketones, this amounts to a one-electron photoreduction, commonly by an electron-rich alkene. This process predominates when the triplet energy of the charge acceptor, E_T is higher than that of an electron-rich donor[4,36]; for phenyl ketones, this corresponds to ET≥ ca. 74 kcal/mol[37]. Kinetic behaviour contrasts that in E. T. quenching in several ways. Firstly, rate constants are in the ca. 10^5 to 10^8 $\underline{M}^{-1}s^{-1}$ range[37]. More significantly, an increase in the rate with decrease of ketone triplet energy and inefficient product formation have been interpreted in terms of the mildly exothermic formation of an inital complex with charge-transfer character[36-38]. The lack of stereospecificity in oxetane photoproducts and the reisolation of isomerised alkenes suggest that the C. T. complex decomposes to a 1,4-biradical intermediate[39]. Amines[40,41] and sulfides[41,42] also quench via C. T. complex formation[9b], by virtue of their lone pair electrons. Quenching by conjugated butadienes may even proceed to a small extent through a C.T. mechanism[37].

C. Extent of Electron Transfer

When ΔG_{ET}, the free energy change for electron transfer, drops below -5 kcal/mol, and if C.T. complex formation is not hindered by bulky substituents on the quencher[37], electron transfer becomes rate-limiting and the rate constant for triplet C.T quenching, k_{CT} can be

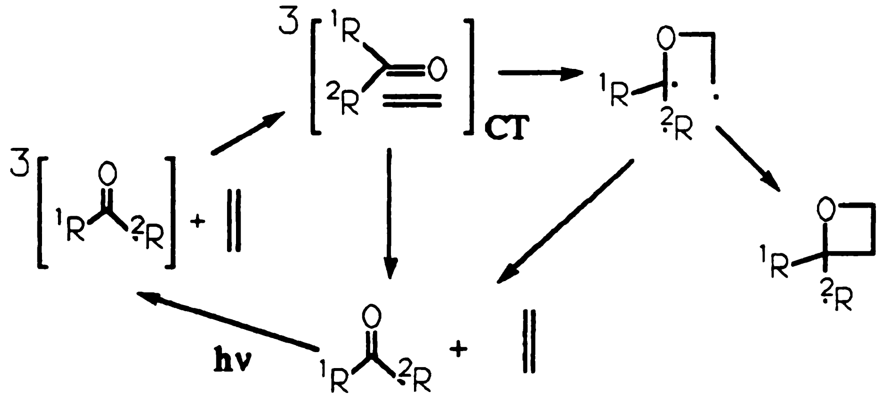


Figure 5. **Mechanism of Charge Transfer Quenching of** n,π^* Triplet State **of Ketones by Alkenes**

directly related to the thermodynamic properties of the C. T. couple through Equation 3, the Guttenplan-Cohen modification of Rehm and Weller's relationship[43] for singlet electron transfer quenching[41a].

$$\ln(k_{CT}) \approx \Delta G_{ET} \approx E(D/D^+) - \Delta^3E_{oo} - E(A^-/A) - T\Delta S \qquad (3)$$

Here, Δ^3E_{oo} and $E(A^-/A)$ are the zero-point triplet energy and ground state reduction potential respectively, of the ketone, $E(D/D^+)$ is the oxidation potential of the charge donor and $T\Delta S$ the entropic contribution to electron transfer. Since $E(D/D^+)$ is equal to the donor ionisation potential, IP_D plus a relatively constant electrostatic factor, the relationship can be reformulated more convienently as Equation 4.

$$\log(k_{CT}) \approx IP_D - \Delta^3E_{oo} - E(A^-/A) + \text{constant} \qquad (4)$$

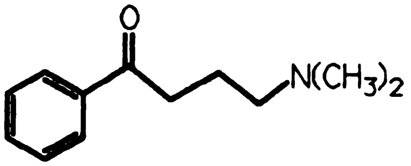
Thus, plots of $\log(k_{CT})$ versus IP_D for various quenchers and a given ketone triplet[34], or $\log(k_{CT})$ versus $-\Delta^3E_{oo} + E(A^-/A)$ for the triplet energies of various ketones and a single quencher[41b] should both show reasonable linear correllation. The former instance has been demonstrated by the studies of Guttenplan and Cohen on the quenching of benzophenone and fluorenone photoreduction by aromatic and aliphatic donors (including some alkenes[41]), as well as similar work by Wagner on the quenching of Type II photoreaction by alkenes[37] and the photoreduction of trifluoroacetophenone by aromatics[44]. The latter type of correllation was verified by Guttenplan and Cohen's studies on the quenching of ketone photoreduction by triethylamine[41].

An increase in solvent polarity has been found to drastically increase the C. T. quenching rate constants for those ketones having π,π^* lowest energy triplets[41b]. However, comparison of the slopes of these and other plots to those from singlet exciplex formation leads to the conclusion that only partial electron transfer is posible in triplet exciplexes.[41a,44].

D. Intramolecular Charge Transfer Quenching

In these kinds of studies, the excited state- and quenching chromophores are separated by a chain of non-transmitting atoms. The difference in reciprocal triplet lifetimes between these species and suitable model systems provides a relative measure of the rate constant for intramolecular C.T. quenching, k_{CT}. Physical contact, manifested through the geometrical- and spatial- requirements of the separating tether, can thereby be proven. Information on the intrinsic quenching abilities in the absence of diffusional constraints can also be obtained.

For example, the triplet lifetimes of phenyl alkyl ketones α, γ and δ-substituted with tertiary amino functions have been shown to depend on the carbonyl-amine separation[45]. A minimum lifetime and a maximum C.T. quenching rate constant, $k_{CT} = 7.2 \times 10^9\ s^{-1}$ were seen[45b] for γ-substituted ketone, 1. A ca. 1.0 M concentration of triethylamine in benzene was necessary to quench valerophenone itself[45] to the same extent. That this reflected a through-space, and not a through-bond phenomenon was demonstrated by Wagner and Scheve in their studies on the 4-benzoylpiperidines, 2. Here, the conformational rigidity of the piperidine ring prevented intramolecular quenching of the benzoyl triplet state[46].



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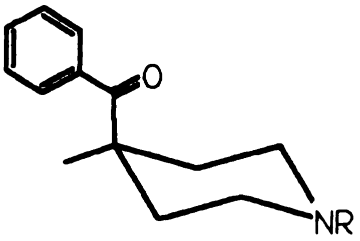
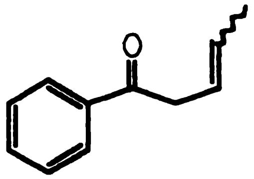


2, R= CH_3, CH_2ph

Also, in the cis- and trans- isomers of compound 3, intramolecular quenching rate constants of $1.5 \times 10^{10}\ s^{-1}$ for each were determined through measurements of quantum yields for isomerisation of the double bond[47] and triplet lifetimes. In compound 4, the quantum yield for formation of Type II photoproducts in benzene was only ca. 0.6% of that for butyrophenone[16], which together with its triplet lifetime implied an intramolecular quenching rate constant of $8 \times 10^{8}\ s^{-1}$. The efficiency of these processes was attested to by the isolation of products from the decomposition of unstable oxetane adducts 5 and the fact that the quenching rates could not be nearly duplicated on a bimolecular level[47].



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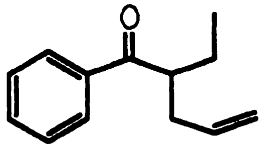

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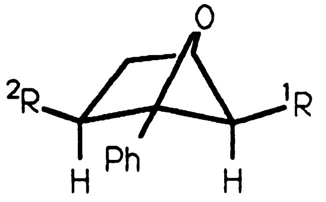
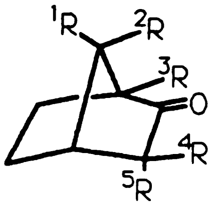


5, $^{1}R = CH_3$, $^{2}R = H$ or $^{1}R = H$, $^{2}R = C_2H_5$

E. Regioelectronic Quenching

Substrates can be devised in which the C.T. quenching moiety enjoys access to different parts of the chromophore. Thus, the extent of quenching can be related to the degree and type of localisation in the excited state.

A classic example is Turro's studies on the quenching of the n,π^* singlet states of alkylated norcamphor derivatives, 6 by electron -attracting and -donating alkenes[48]. Here, the rate of quenching by trans-1,2-dicyanoethylene was shown to be dependent on alkyl substitution which blocked access to the areas above and below the carbonyl plane, while quenching by cis-1,2-dimethoxyethylene was limited by those alkyl groups which hindered approach from the sides of the carbonyl group.

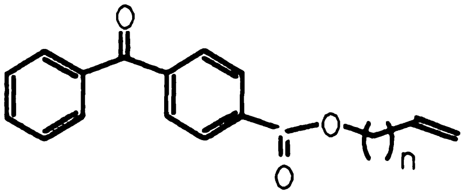


6, ^1R - ^5R= alkyl or H

This is understandable, since in a C.T. mechanism, dicyanoethylene must quench through the half-filled π^* orbital above or below the carbonyl plane, and dimethoxyethylene should interact by means of the half-vacant oxygen n-orbital in the plane. Thus, quenching rates by trans-1,2-dicyanoethylene were least for those photosubstrates where ^2R, ^4R or ^5R= CH_3 (^1R and ^3R= H or CH_3) and quenching by cis-1,2-dimethoxyethane was slowest for photosubstrates where ^3R or ^5R= CH_3 (^1R, ^2R and ^4R= H or CH_3).

In a significant intramolecular case, Winnik measured the phosphorescent lifetimes, τ_P for a series of ω-alkenoxy p-benzoylbenzoate esters, 7 having n,π^* lowest triplet excited states in acetic acid as a function of tether length[49].

A moderate drop in τ_P, relative to 4-carbomethoxybenzophenone was observed[49a] from n= 6 (k_{CT}= 1.3×10^4 s^{-1}) up to n= 8 (k_{CT}= $2.3 \times 10^5 s^{-1}$); thereafter τ_P decreased rapidly until n= 12 (k_{CT}= 7.9×10^5) after correction for bimolecular quenching by the ground state ketone[49b]. Simple molecular models demonstrate that n= 8



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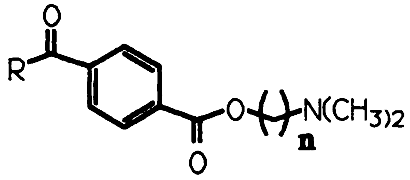
corresponds to the smallest chain length at which the olefinic moiety can come within ca. 1 Å of the ketone carbonyl and still maintain the trans-coplanar ester conformation; contact with the aromatic ring is insufficient[49]. Winnik has pointed out that this and the sharp drop in phosphorescent lifetime with tether length implied that the alkene must be well within the sum of the van der Waal radi for itself and the carbonyl for effective quenching to occur. Up to n= 12, quenching is enhanced by an increase in the number of proximate olefin-ketone carbonyl conformations. Beyond this chain length, the entropy of the total number of conformations available to the flexible ω-alkenyl chains gradually overcomes the number of favourable quenching interactions[49b].

Alternately, the absence of strong intramolecular quenching of the phosphorescence of the 2-(N,N-dimethylamino)ethyl p-benzoylbenzoate ester, 8 in CCl_4 has been attributed by Wagner and Siebert to the inaccessibility of the tethered amine to the n,π^* lowest triplet state[50]. It is interesting to note that although much slower than the rate constant for intermolecular quenching of benzophenone with triethylamine in benzene[51], 2.3×10^9 $\underline{M}^{-1}s^{-1}$, the rate of intramolecular quenching here, 1 x 10^{5} s^{-1} was still comparable to that observed in Winnik's esters. This apparent anomaly reflected the greater reducing ability of tertiary amines than primary olifines[52].

On the other hand, C.T. quenching studies on the Type II photoelimination of ω-(N,N-dialkylamino)alkyl *p*-valerylbenzoate esters *9* in acetonitrile[50] showed much greater rates, k_{CT}= 5.1 x 10^{8} and 6.6 x 10^{8} s^{-1} for n= 2 and 3, respectively, against 1.6 x10^{10} $\underline{M}^{-1}s^{-1}$ for quenching of the methyl ester homologue with triethylamine. This contrast was thought to be a consequence of the locality of the 4'-acylbenzoate chromophore's π,π^{*} lowest triplet state on the aromatic ring, within reach of the tethered amine. A further endorsement of this concept was provided by the *meta* isomer of *8* (n= 2), which had a n,π^{*} lowest triplet state and showed a triplet lifetime compareable to that of its methyl ester homologue[50].



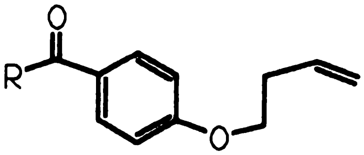
8, R= C_6H_5; n= 2

9, R= $^{n}C_4H_9$; n= 2, 3

IV. INTRAMOLECULAR TRIPLET AROMATIC PHOTOCYCLOADDITION

A. *Acylphenyl Alkenyl Ethers*

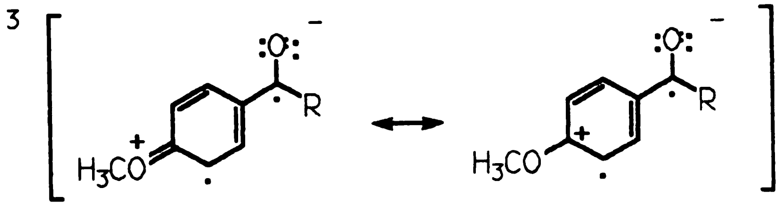
The Type II photokinetics of the π,π^* lowest triplet state of the acylphenyl alkenyl ethers, 10 were also recently examined by Wagner and Nahm for evidence of intramolecular C.T. interactions[53]. The simple *para*-3-butenyl ether and its *ortho* isomer (both R= $^nC_4H_9$) showed values of 8.9 x 10^7 and 3.3 x 10^7 s^{-1}, respectively.



10, R= CH_3, C_4H_9

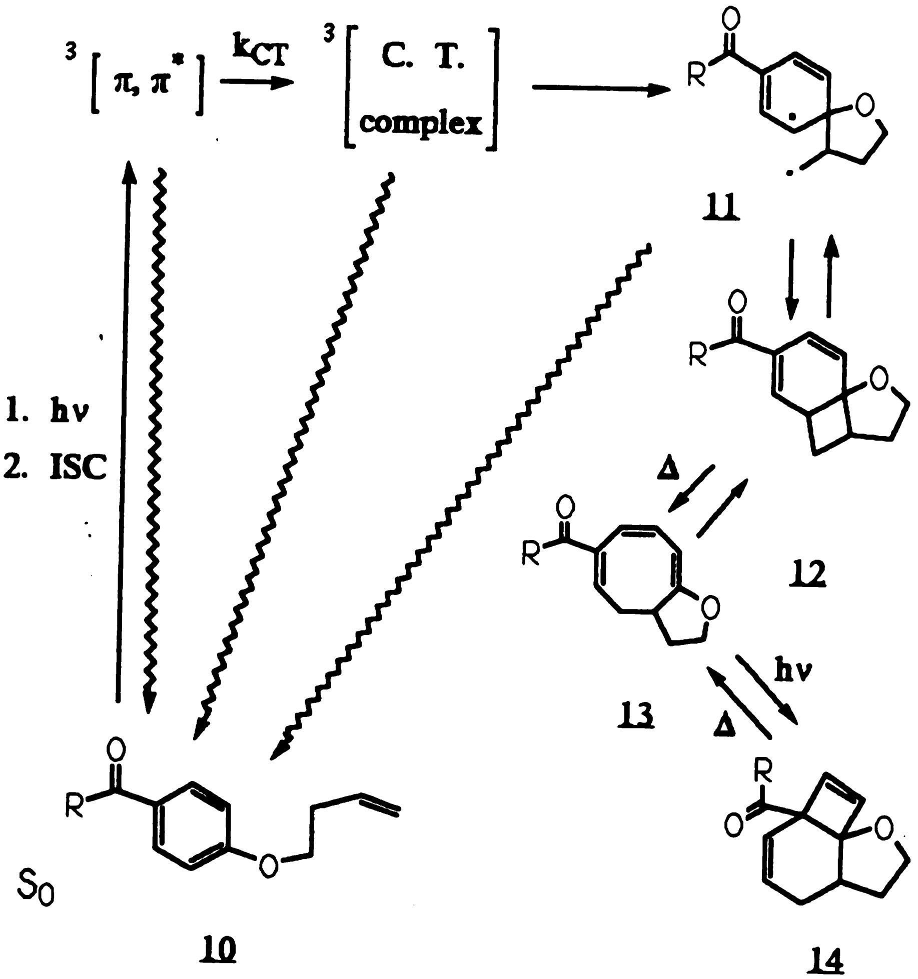
Compared to intramolecular C.T. quenching of n,π^* triplet states by olefines, the magnitude of this effect was between those of the benzophenone alkenyl esters[49], 7 and the β-vinyl phenyl ketones[47], 3 and 4. This may have been a consequence of the intrinsically different C.T. quenching efficiencies of n,π^* and π,π^* triplet states and/or the limitations imposed by tether length and geometry and distance from the quenched chromophore.

Further light was shed on the nature of the lowest triplet state in the alkenyl ethers by the much lower quenching rates exhibited by the *meta* isomer of 10. Although posessing a π,π^* lowest triplet state, in analogy to m-methoxyphenyl alkyl ketones [21], charge-separated resonance hybrids are excluded from its triplet state. This, and the great



enhancement in C.T. rate constants upon alkyl substitution in the double bond of the para isomer, implied that this process was aided by the development of a partial positive charge in the 4'-aromatic position of the excited state.

Other kinetic phenomena made definite predictions about the quenching mechanism. First, the rates of C. T. quenching in the para ether and of cis -> trans isomerisation of the double bond in the p-cis-3-hexenyl ether (R- $^{n}C_4H_9$) far exceeded those for Type II photoelimination in the methyl ether homologue. In analogy to the reversible addition of olefins to n,π^* ketone triplet states [39,54], this was thought to imply the formation of a spiro-cyclopentyl 1,4-biradical intermediate **11**, from the C. T. complex. Like the intermolecular[54] and intramolecular[47] [2+2] photocycloaddition leading to oxetane formation[54], closure of the biradical was found to give initialy bicyclo[4.2.0]octa-2,4-diene type products[53a], **12**. Analogous reactivity was exhibited by the ortho ethers[53b], as well as homologues of **9** and ortho-**9** which were substituted with methyl groups on the double bond[53]. The combination of biradical revertibility and a kinetically predominant quenching mechanism made for low quantum yields but good (ca. 70%) chemical yields.



With few exceptions, however, the inital cycloadducts were unstable to ring-opening via 3,3-sigmatropic rearrangement[55], giving the corresponding cycloöcta-1,3,5-trienes 13, as also seen in simpler all-carbon ring systems[56]. Absorption of a second photon of light then initiated a [2+2] electrocyclic ring closure, which produced exo-1-

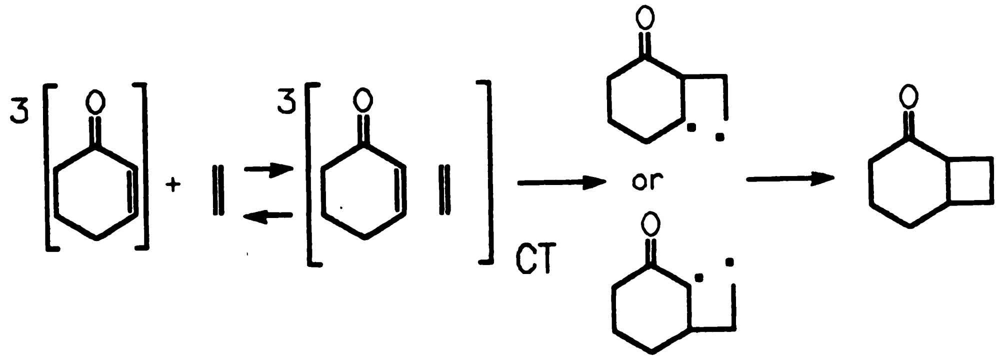
acetyl-5-oxabicyclo[7.2.0.0^{4,8}]undec-2,11-dienes, 14. These compounds were themselves unstable to the octatrienes, and thermally reverted to those compounds via a supposedly non-concerted process.

The various 4-pentenyl ethers of the ortho- and para- isomers also formed compareable cycloadducts, but with much lower quenching rates. No similar photoproducts were detected from the meta 3-butenyl ethers.

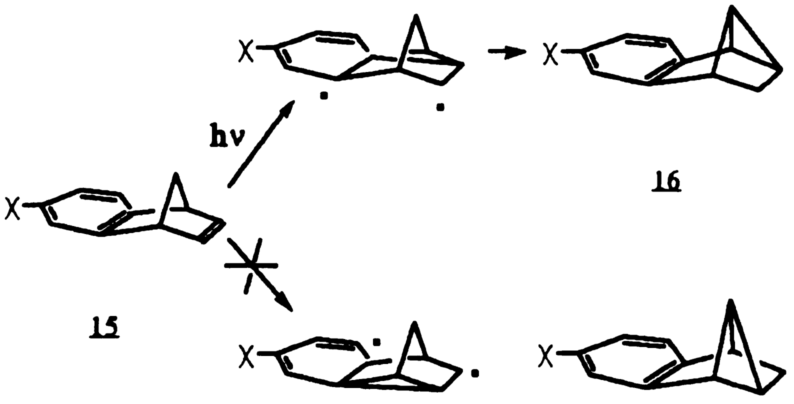
B. Literature Precedents

Since this Thesis concerns some aspects of the generality of this unusual reaction, a diversion to compare conceptually related reactions is warranted.

Kinetically, the previously discussed C.T. quenching and photocycloaddition resembles the inter- or intra- molecular reaction of triplet excited cyclic enones with olefins; both proceed by rapid C. T. complex formation followed by stepwise, reversible bond formation to produce fused cyclobutanes through a 1,4-biradical intermediate[57a] or return to the ground state photosubstrate.

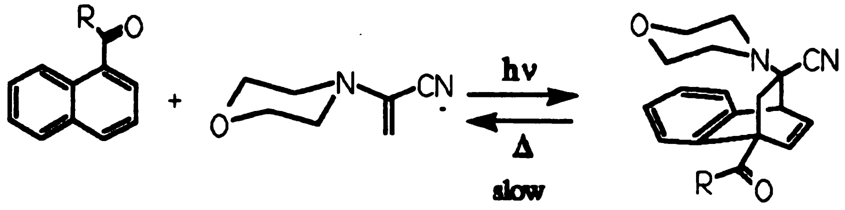


The inital formation of an ipso bound biradical in the 4'-acylphenyl ethers --para to the acyl moiety-- is also thought to be in accord with molecular orbital calculations[58] predicting large LUMO coefficients, and spectroscopic evidence[59] of high (triplet) electron density on the para position of conjugatively electron-accepting benzenoids. These predictions were also bourne out by Paquette's studies on the di-π-methane rearrangement of benzanorbornadienes meta-substituted with similar groups, 15 [60a]. The rate-determining step of this reaction is thought to be the formation of a biradical from attack of the fused aromatic position onto the vinyl group[61]. Thus, in principle, two regioisomers might be expected from irradiation of 15- however, only 16 was formed, via attack of the aromatic π bond electrons from the position para to the conjugatively electron accepting group. A predicted preference[58] for the opposite regioselectivity from analogous photosubstrates substituted with conjugatively electron-donating groups has also been experimentally confirmed[60b].



$X= C(O)CH_3, CN, CO_2C_2H_5, NO_2$

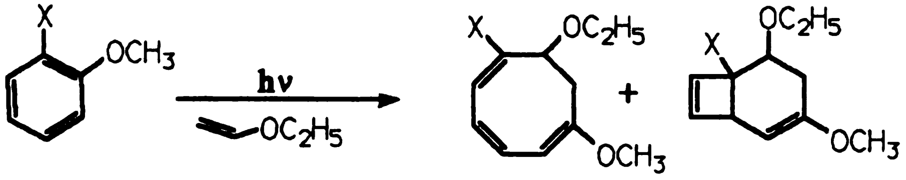
Also supporting this same sort of excited state electronic distribution is one of the few other examples of photocycloaddition of an alkene onto a π,π^* triplet aromatic. In 1985, Döpp documented the efficient formation of thermally unstable 1,4-cycloadducts, 17 between 1-acylnaphthalenes and α-morpholinoacrylonitrile[62]. However, this olefin was highly activated, and the addition mechanism is not entirely clear.



17, R= H, CH_3, ph

Formation of ortho photocycloadducts between olefines and singlet excited benzene derivatives is also possible under certain circumstances, although generalisations in reaction -outcome and -mechanism are difficult[63]. The *ortho* mode is usually favoured when the aromatic is conjugatively electron withdrawing[64a]. Electron-donating olefins are also known to yield exclusively *ortho* photocyloadducts with benzene[64b,c], and with aromatics having dual donor-acceptor properties[64d]. The mechanism for their formation appears to involve ground state complexes whose geometry can be partially correlated with the electronic properties of the olefin[64b]. Because orbital symmetry rules for singlet benzene forbid a concerted mechanism[64e] as well as because the quantum yields for cycloaddition increase with solvent polarity[64b], it is thought to occur by stepwise bond formation through a C. T. complex. However, in the absence of appropriate substituents which polarise the aromatic ring electron density, great regioselectivity is not observed[64a-c].

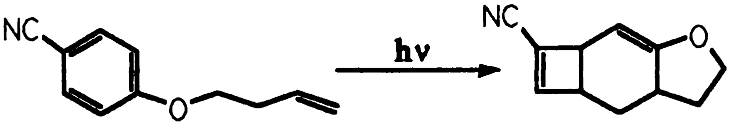
One case in point is the work of Gilbert and co-workers on the irradiation of *o*-methoxy -benzonitrile and -methyl- benzoate 18 in neat ethyl vinyl ether[64d]. The rearranged products from cycloaddition, 19 and 20, formed through a rearrangement like that of the acylphenyl alkenyl ethers, were isolated in high chemical yield.



18, X= CN, CO_2CH_3 19 20

The meta and para isomers of the -CN homologue also underwent compareable photocycloadditions, but with less regioselectivity; adducts resulting from addition of the ethoxy end of the enol to the -CN bearing aromatic carbon were also formed in compareable amounts[64d]. Addition of other alkenes to the methoxybenzonitriles gave cycloadducts from the ortho- (both regioisomers), meta- (vide infra) and other additon modes[65].

The p-(3-butenyl)benzonitrile 21 also undergoes smoothly the intramolecular version of this reaction to form the expected biphotonic product 22 upon prolonged irradiation[66].

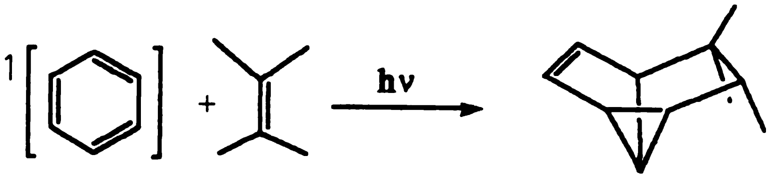


21

22

The ortho isomer of 21 also reacted, as did the p-carbomethoxy homologue of the nitrile, albeit at reduced rates. The lack of reactivity from the meta isomer here may have reflected geometrical, and not electronic limitations on the singlet C. T. complex or biradical[66].

Alkenes can also undergo meta photocycloaddition to singlet benzene. This pathway predominates for olefines and benzene derivatives having similar electron affinities[63]. It has been shown to proceed probaly through a symmetry-allowed, essentially concerted process; excited state exciplexes, not ground state C.T. complexes are possibly implicated[64d]. The initally formed tricyclo[3.3.0.0^{2,8}]oct-3-ene type systems, 23 have found wide use in Natural Product Synthesis[67].



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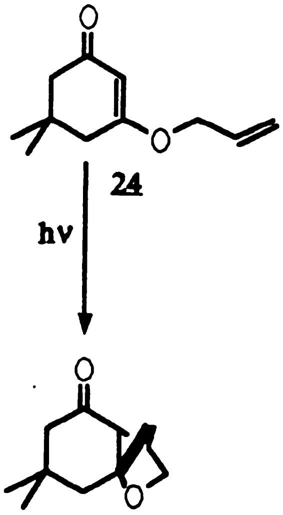
Finally, a comparison of the effects of tether -length and -constitution on the relative efficiencies of photocycloaddition and C. T. quenching is necessary.

Wagner and Nahm described a maximum of C. T. quenching- and photocycloaddition- quantum yields for three-atom separation of the double bond from the acylphenyl chromophore[53]. No quenching was observed for chain lengths greater than four atoms. These systems showed a strong preference for formation of a five-membered ring biradical intermediate. This trend has also been documented through the "rule of five" in intramolecular enone-olefin photocycloaddition[57b,c] as seen below for the stereoselective reactions of 24 and 25 , the quantum yields for intramolecular meta photocycloaddition of ω-phenyl-1-alkenes[64], the stereospecificity of oxetane formation from the γ,δ-unsaturated phenyl ketones[47] (cf. compound 5) and intramolecular naphthonitrile-alkene singlet exciplex formation[68]. It is also parallelled by ground state radical[69a]- and



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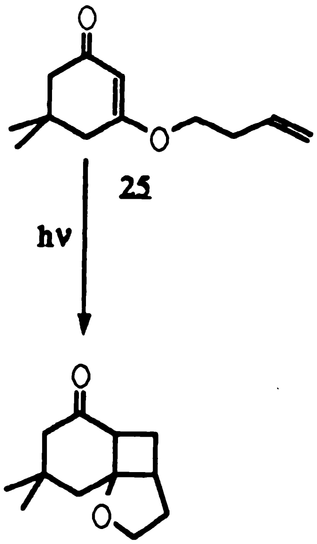

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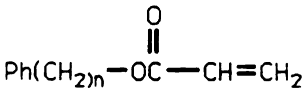
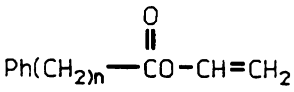
carbonium[69b]- cyclisation studies. It should be noted, however, that interactions requiring chain lengths greater than five atoms were seen in Winnik's ω-alkenyl esters, in Siebert's ω-amino esters, in δ-dialkylaminobutyrophenone, and are not impossible in enone photocycloaddition[57b]. As well, excimer formation and self-photodimerisation of >four-atom linked bis-anthracenyl singlet substrates has been observed[70].

Intramolecular photocycloaddition in the acylphenyl alkenyl ether, as well as in the singlet ortho and meta cases occurs efficiently through either an all-carbon- or ether- tether[66,71] (substituent effects on the nature of the lowest excited state notwithstanding). The introduction of an ester function into the longer tethers of the ω-amino valerophenone esters[50] but especially in Winnik's compounds[49] was not detrimental to their quenching abilities. In singlet meta cycloaddition substrates, however, the presence of ester functions in



$Ph(CH_2)_n{-}O\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2$

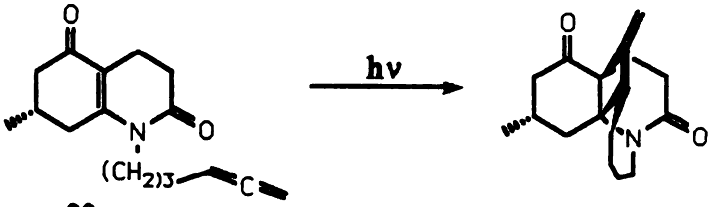
26, n= 1, 2 or 3



$Ph(CH_2)_n{-}\overset{\overset{O}{\|}}{C}O{-}CH{=}CH_2$

27, n= 1, 2 or 3

the tether adjacent to the olefin such as in 26 or 27 drastically lowers reactivity[55]. On the other hand, enone photocycloadditions have been implemented through a variety of tether linkages, including a conformationally restraining one like seen for 28[72].



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V. KINETIC FORMULATIONS

The following is a cursory description of the relations which will be used to derive the Type II steady state kinetic parameters used in this Thesis.

A. Quantum -Yields and -Efficiencies

The quantum yield of a photochemical process, Φ is the ratio of molecules which can undergo that process to the total number of photons absorbed by the concerned photosubstrate[73]. In terms of photoproduct concentration [P] and light intensity absorbed, I_a, Φ is defined in Equation 6. Experimentally, I_a may be determined from the Beer-Lambert

$$\Phi = [P]/I_a \tag{6}$$

law[74].

Kinetically, quantum yields are described in terms of the product of the individual quantum efficiencies, ϕ_i of each step along the pathway leading to the final, detectable species. The ϕ_i are defined as the productive fraction of net unimolecular decomposition rates from each intermediate state.

Thus, the observed quantum yield for formation of Type II cleavage protoproducts from a phenyl alkyl ketone, Φ_{II} is defined in Equation 7 as the product of ϕ_{isc}, ϕ_H and P, the quantum efficiencies of singlet -> triplet intersystem crossing, hydrogen abstraction, and partitioning of the resulting 1,4-biradical towards cleavage products.

$$\Phi_{II} = \phi_{ISC} \cdot \phi_H \cdot P \tag{7}$$

In spite of the number of independent unknowns, Equation 7 is easily evaluated. First, $\phi_{ISC} = 1.0$ for phenyl alkyl ketones[2]. Also, in the presence of a Lewis base, return of the 1,4-biradical to the ground state photosubstrate is blocked[16], and so P reduces to $k_{cl}/(k_{cl} + k_{cy})$, a relatively constant term for constant substitution at the γ position[10c]. Now the maximised quantum yiels for cleavage product formation, Φ_{MAX} is represented by Equation 8.

$$\Phi_{MAX} = \phi_H \cdot k_{cl}/(k_{cl} + k_{cy}) \tag{8}$$

B. Lifetimes

The intrinsic lifetime of a transient species, τ, is defined as the reciprocal of the sum of the rate constants for all intramolecular processes accessible to it[73], Equation 9. For phenyl alkyl ketones

$$1/\tau = \Sigma\, k_d \tag{9}$$

capeable of hydrogen abstraction, $\Sigma\, k_d$ includes k_{ir}, k_H, k_{CT} etc. The intrinsic lfetime of such a photosubstrate is then related to ϕ_H and k_H, the actual rate constant for hydrogen abstraction from the triplet state, through Equation 10. Substitution of Equation 10 into Equation

$$\phi_H = k_H \cdot \tau \tag{10}$$

8 and defining the experimentally determined rate constant for formation of cleavage products, $k_{II} = k_H \cdot k_{cl}/(k_{cl} + k_{cy})$, then yields Equation 11, which, with knowledge of τ, provides an experimentally

accessible rate constant for Type II photocleavage reactivity[13,16].

$$\Phi_{MAX} = k_{II} \cdot \tau \tag{11}$$

C. Stern-Volmer Kinetics

The lifetime of an excited state can be experimentally determined by monitoring the effects of a state specific quencher, Q, on the extent of a respectively state specific photoprocess according to the Stern-Volmer equation[73,75]. For phenyl alkyl ketones undergoing Type II cleavage[8,13], this amounts to Equation 12, where Φ is the quantum

$$\Phi^{o}/\Phi = 1 + k_q \cdot [Q] \cdot \tau \tag{12}$$

yield in the presence of a known concentration of quencher, Q and $\Phi^{o} = \Phi_{II}$. Evaluation of τ then follows from the slope of a plot of Φ^{o}/Φ versus [Q] and k_q for a quencher quenching[76,77] at or near the diffusional limit[34].

VI. RESEARCH GOALS

In this Thesis, the Type II photokinetics of compounds analogous to Siebert's 4'-valeryl benzoate esters, but bearing terminal olefinic tethers, were initally studied for evidence of intramolecular C.T. quenching. Irradiations of some of the corresponding 4'-acetyl benzoate esters were also examined for photocycloadducts comparable to those from the 4'-acylphenyl alkenyl ethers. The results of those experiments prompted the scrutiny of two other classes of keto-esters:

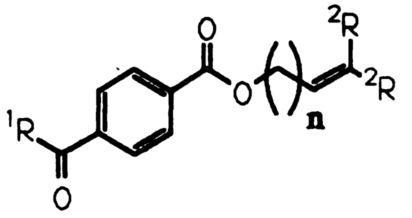
Firstly, the photokinetics of ω-alkenoate esters of 4'-acylphenols, wherein the "direction" of the tethering ester moiety was "reversed", were studied. The triplet lifetimes of these photosubstrates were compared to those of the yet-unmeasured 4'-acylphenyl acetate esters. Thus, information on the effects of yet another aromatic substituent on Type II reactivity was obtained as a bonus.

Secondly, the possiblity of photocycloadducts from acetophenones having both a _para_-methoxy group, to favour a π,π^* lowest triplet state, and a _meta_ benzoate-linked tether was investigated.

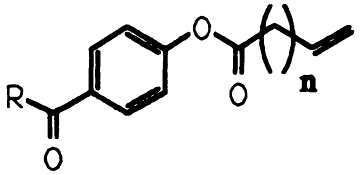
RESULTS

I. COMPOUNDS STUDIED

The Type II photokinetic- and quantum yield- parameters of the 4'-valeryl allyl-, 3-methyl-2-butenyl- (prenyl-) and 3-butenyl-benzoates 29b, 30b and 31b in benzene were measured. Also examined in this regard were the 4'-butyrylphenyl -3-butenoate and -4-pentenoate esters, 32b and 33b, in 4:1-methanol: benzene.

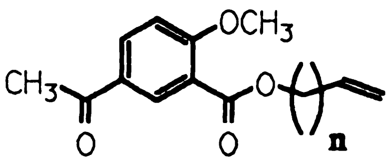


29a, n= 1; ^{1}R= CH_3; ^{2}R= H
29b, n= 1; ^{1}R= $^{n}C_4H_9$; ^{2}R= H
30b, n= 1; ^{1}R= $^{n}C_4H_9$; ^{2}R= CH_3
31a, n= 2; ^{1}R= CH_3; ^{2}R= H
31b, n= 2; ^{1}R= $^{n}C_4H_9$; ^{2}R= H



32a, n= 1; R= CH_3
32b, n= 1; R= $^{n}C_3H_7$
33b, n= 2; R= $^{n}C_3H_7$

Irradiations of the corresponding acetophenone derivatives, 29a, 31a and 32a, as well as the 5'-acetyl-2'-methoxy -allyl- and -3-butenyl benzoate esters 34a and 35a were also followed by ^{1}H NMR spectroscopy.



34a, n= 1

35a, n= 2

II. SYNTHESIS

Methyl trans-crotonate was prepared by Fisher esterification[78] of an excess of crotonic acid with methanol in the presence of a catalytic amount of sulfuric acid[79].

The benzoate and alkenoate ester photosubstrates and calibration standards 29 - 35 were obtained from the corresponding carboxylic acids and alcohols. Their structural identities were confirmed by their ^{1}H- and ^{13}C- NMR-, IR- and mass- spectra. All compounds were of greater than 98% purity by gas chromatography, except where noted.

The 4'-acylbenzoic acids were prepared by displacement of fluoride by cyanide from the 4'-acylfluorobenzenes[80] followed by basic hydrolysis, according to the overall method used by Siebert[81]. In the case of 4'-acetybenzonitrile, basic hydrolysis gave an unacceptably low yield of 4'-acetylbenzoic acid, and so the hydrolysis was carried out under acidic conditions[82]. The physical properties of the benzoic acids were identical to those reported earlier[81,82].

The 4'-acyl allyl benzoates 29 were obtained from reaction of the 4'-acylbenzoyl chlorides with allyl alcohol[83].

The acid chloride technique effected partial positional isomerisation of the double bond in the 4'-acyl prenyl benzoates 30, and so they were prepared in gas chromatographically pure condition from the 4'-acyl potassium benzoates and diethylprenylsulfonium tetrafluoroborate[84] using a modification of the procedure of Julia[85].

The 4'-acyl 3-butenyl benzoates 31 were also unsuited for preparation via the acid chlorides; they were obtained instead from the 4'-acyl potassium benzoates and excess 4-bromo-1-butene in 1:1-hexamethylphosphoric triamide:ethanol[86]. The bromoalkene was prepared by an established means[87].

The 4'-acylphenyl esters were obtained from the appropriate 4'-acylphenols and carboxylic acids or anhydrides. The 4'-acetylphenol was commercially available, while the other 4'-acylphenols were formed in one step from butyric or valeric acid, phenol and polyphosphoric acid according to a procedure adapted from the literature[88]. Their spectroscopic and physical properties agreed with those already reported[89].

The acetate esters were prepared by Schotten-Baumen esterification of the phenols with acetic anhydride in cold sodium hydroxide solution[90]. Physical- and/or spectroscopic- properties of the acetate esters agreed with those in the literature[91,92], when reported.

The 3-butenoate and 4-pentenoate esters 32 and 33 as well as 4'-acetylphenyl trans-crotonate (vide infra) were prepared by coupling the appropriate 4'-acylphenols and alkenoic acids with dicyclohexylcarbodiimide and 4'-N,N-dimethylaminopyridine[93]. The 3-butenoic acid was commercially available and 4-pentenoic acid was prepared by a known procedure[94].

The spectral properties of the 3-butenoate esters (^{1}H- and ^{13}C-NMR, IR) agreed with their anticipated structures and after simple work-up showed them to be of greater than 98% purity, the major impurity being their trans-crotonate isomers. The relative amounts of each isomer were initally assayed from the ratio of signal areas in their ^{1}H NMR spectra attributable to protons unique to the 3-butenoate and trans-crotonate[95] residues, at δ3.29 (doublet of triplets, 2H, $-C(O)C\underline{H}_2CH{=}CH_2$) and δ1.96 (doublet of doublets, 3H, $-C(O)CH{=}CHC\underline{H}_3$), respectively. The esters were not stable under gas chromatographic conditions (15 m DB-1 column; column temperature= 150°) and all attempts to remove these impurities (flash chromatography from silica- and neutral alumina, ultra high vacuum distillation from silanized glassware, Diels-Alder reaction with cyclopentadiene) were fruitless. They were relatively stable as neat oils at ca. 0° in silanized glassware.

The proportion of crotonate ester of 32b increased rapidly in the 4:1-methanol:benzene photolysis solutions- to ca. 4% within four hours at room temperature (generally the time required to prepare and degas the photolysis solutions) or ca. 50% overnight. However, control experiments indicated that no further isomerisation of photosubstrate 32b or photoproduct 32a occurred under the actual conditions (ca. 0°) and time frame (ca. 2 h) of the irradiations. The amount of 32b-crotonate in the photolysis solutions was assayed by reverse phase HPLC

(UV detection at 250 nm; solvent gradient program (% acetonitrile in water; flow rate= 1.0 ml/min.): 36%, then at 15 min. to 50%, then at 22 min. to 36%). The 4'-acetylphenyl trans-crotonate eluted at 10.5 min, 0.6 min after 32a. Therefore, the peak at 27.2 min. which increased with time in area at the expense of the area of the peak from 32b at 26.0 min. was assumed to arise from 32b-crotonate. See "Photolysis"/ "Results" and "Photolysis Procedures"/ "Experimental" Sections for further details.

The 4'-butyrylphenyl 4-pentenoate esters 33 were stable compounds and were obtained without complication.

The alkenyl esters of 5'-acetyl-2'-methoxybenzoic acid 34a and 35a were synthesized by coupling the carboxylic acid and appropriate alcohol with dicyclohexylcarbodiimide and 4'-N,N-dimethylaminopyridine[93]. The 5'-acetyl-2'-methoxybenzoic acid was prepared by a known procedure from acetyl salicylic acid[96,97].

III. PHOTOLYSIS

A. Photokinetic and Quantum Yield Experiments

1. Photoproduct Identification

All acetophenone photoproducts were identified by comparison of their gas chromatographic- or HPLC- retention times to those of authentic samples. The identity of the 4'-butyryl- and 4'-valerylphenyl acetate photoproduct was also confirmed by analogy to the earlier characterisation of the 4'-butyrylphenyl acetate photoproduct by Pitts[19].

2. Stern-Volmer Quenching Plots

Degassed and vacuum-sealed benzene or 4:1-methanol:benzene solutions containing 0.03 M ketone and varying amounts of 2,5-dimethylhexa-2,4-diene (DMHD) or methyl trans-crotonate quenchers were irradiated at 313 nm in a merry-go-round apparatus to 2 - 12% conversion. Linear Stern-Volmer plots of Φ^o/Φ versus quencher concentration were derived from the ratio of concentrations of acetophenone photoproduct measured for each solution. The slope of these plots was equal to $k_q\tau$, where k_q was the rate of quenching of the triplet ketone and τ is its lifetime[76,77]. The values collected in Tables 1 - 3 were taken from runs agreeing to within ca. 10% of each other and their Stern-Volmer plots for typical runs are summarised on Figures 6 - 8 and 11. The line calculated from similar data for 4'-carbomethoxyvalerophenone reported by Siebert[23,81] is included in Figure 6 for comparison.

3. Quantum Yields

The quantum yields for the formation of the acetophenone photoproducts were measured by the irradiation of degassed benzene solutions containing 0.1 M valerophenone actinometer in parallel with 0.03 M ketone photosubstrate[16]. Conversion of valerophenone was kept

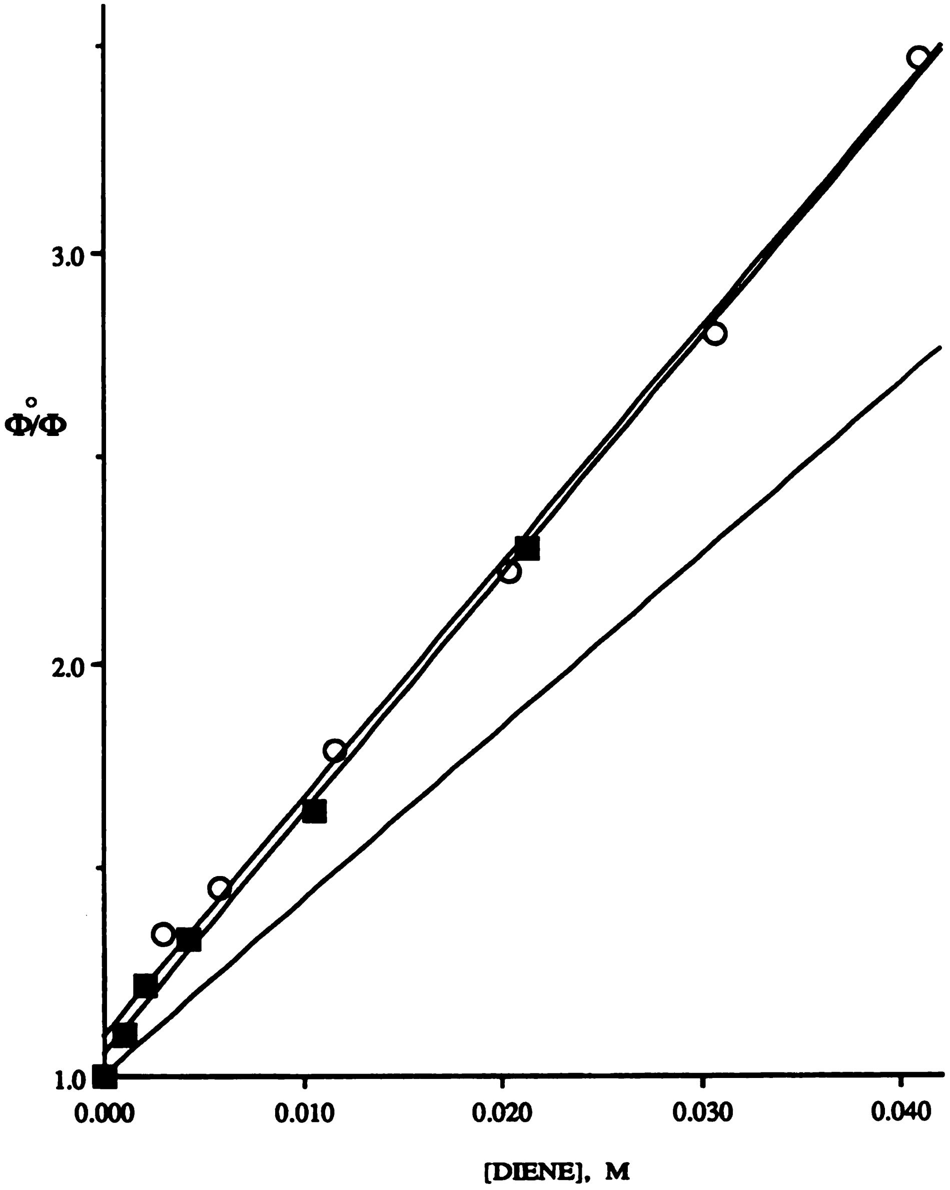


Figure 6. **Stern-Volmer Plot for Quenching of Acetophenone Formation from 4'-Valeryl Alkenyl Benzoate Esters with 2,5-Dimethyl-2,4-Hexadiene in Benzene.** Data for line equation of 4'-carbomethoxyvalerophenone from Doctoral Dissertation of E. Siebert included for comparison. Legend: allyl ester: open circle; 3-butenyl ester: closed circle; methyl ester: no marks.

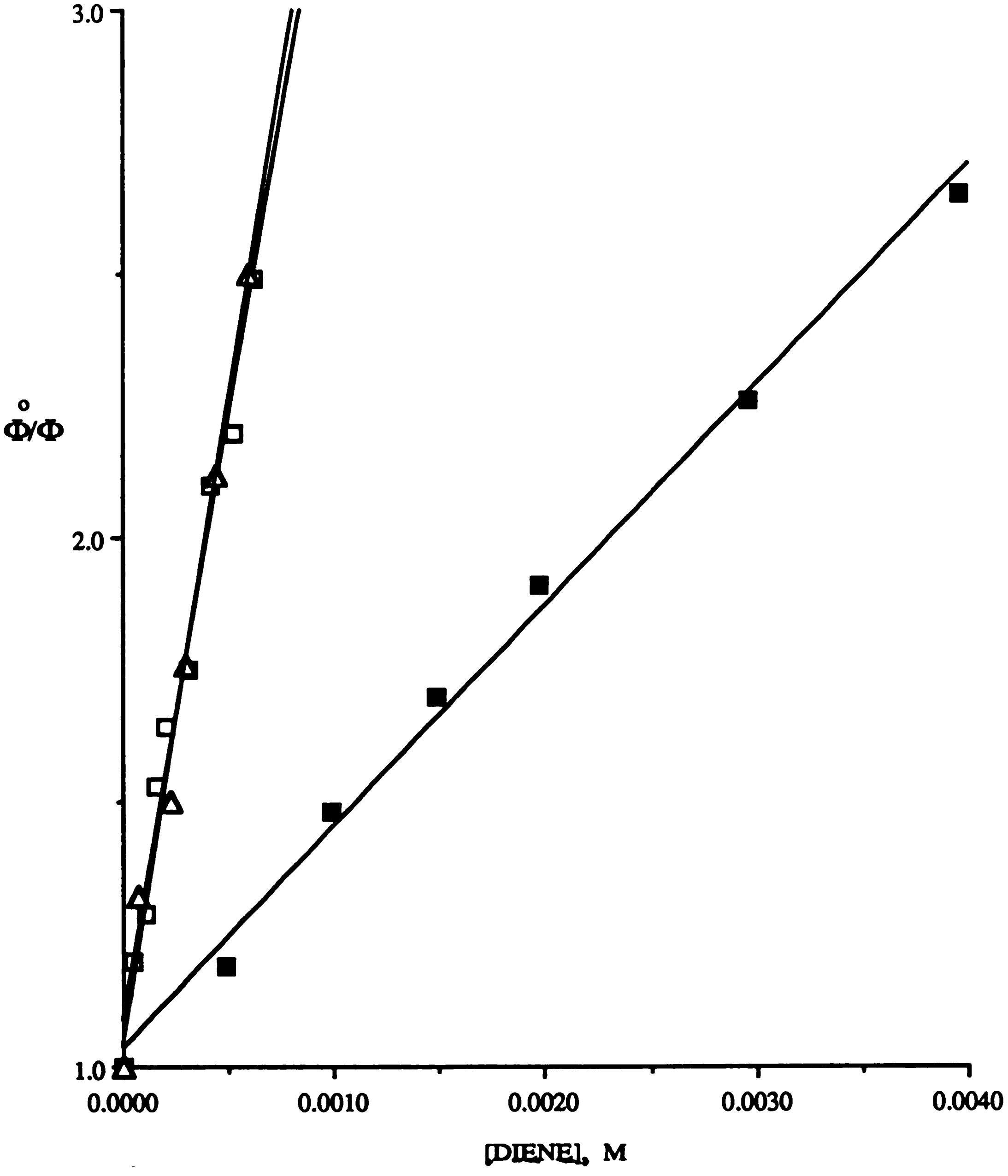


Figure 7. **Stern-Volmer Plot for Quenching of Acetophenone Formation from 4'-Butyrylphenyl Alkenoate Esters with 2,5-Dimethyl-2,4-Hexadiene in 4:1 - Methanol:Benzene.** Legend: 3-butenoate ester: closed square; 4-pentenoate ester: open triangle; acetate ester: open circle.

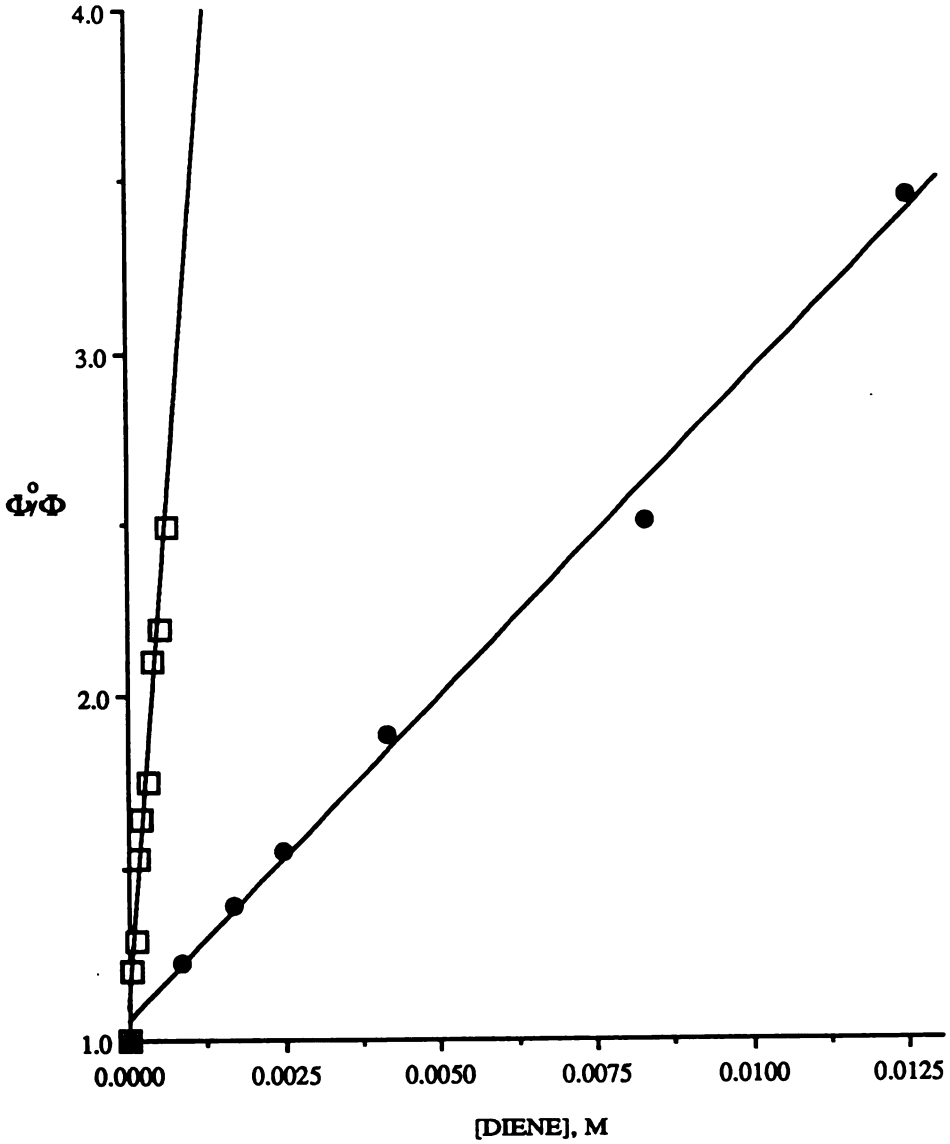


Figure 8. Stern-Volmer Plot for Quenching of Acetophenone Formation from 4'-Acylphenyl Acetate Esters with 2,5-Dimethyl-2,4-Hexadiene in 4:1 - Methanol:Benzene. Legend: 4'-butyrylphenyl acetate: open square; 4'-valerylphenyl acetate: closed circle.

to ca. 3% or lower. Quantum yields are reported with Stern-Volmer data in Tables 1 - 3.

Table 1. Photokinetic Parameters for Quenching of Alkenyl 4'-Valerylbenzoate Esters with 2,5-Dimethyl-2,4-Hexadiene in Benzene

Photosubstrate	Alkenyl moiety	Φ_{II}	$k_q\tau, \underline{M}^{-1}$
$\underline{p}$-CO_2CH_3VP[a]	CH_3	0.19	42
<u>29b</u>	$CH_2CH{=}CH_2$	0.18±0.03	55±3
<u>30b</u>	$CH_2CH{=}CH(CH_3)_2$	0.25±0.01	----
<u>31b</u>	$(CH_2)_2CH{=}CH_2$	0.181±0.001	61±1

a: <u>para</u>-carbomethoxyvalerophenone; data taken from Doctoral Dissertation of E. Siebert.

4. Limiting Quantum Yield

The intercept of the plot of $1/\Phi_{II}$ versus concentration[13,50] of 4'-butyrylphenyl 3-butenoate, shown in Figure 9, was taken as $1/\Phi_{LIM}$, where Φ_{LIM} was defined as the quantum yield for Type II photoelimination in the absence of intermolecular quenching[50,53a]. This quantity is listed in Table 2.

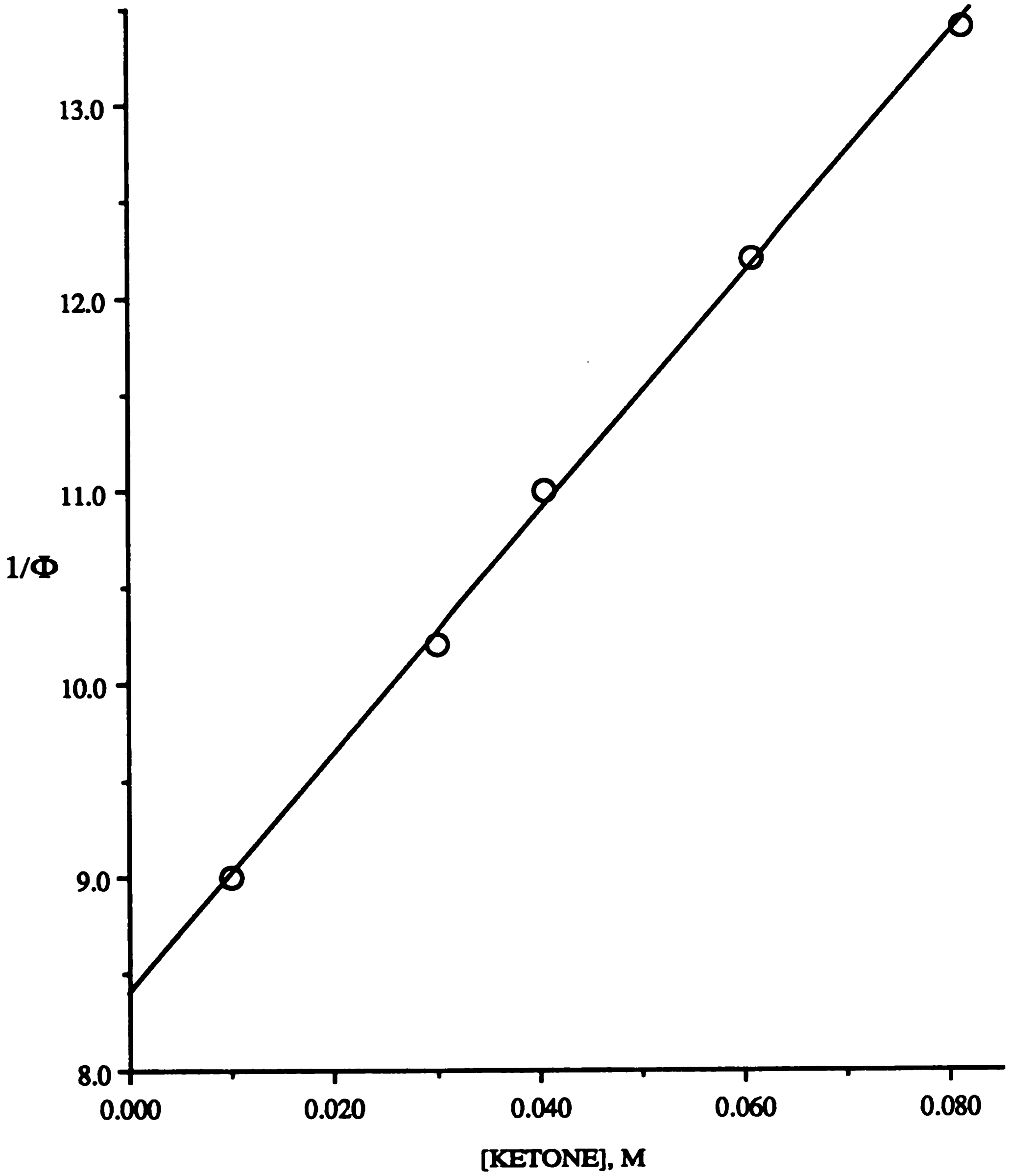


Figure 9. Dependence of Reciprocal Quantum Yield of Acetophenone Formation from 4′-Butyrylphenyl 3-Butenoate on Ketone Concentration in 4:1 - Methanol:Benzene.

Table 2. **Quantum Yield- and Photokinetic- Parameters for Quenching of 4'-Butyrylphenyl Alkenoate Esters wih 2,5-Dimethyl-2,4-Hexadiene in 4:1 - Methanol:Benzene**[a]

Photo-substrate	Acid Residue	Φ_{II}	Φ_{LIM}	$k_q\tau$, $\underline{M}^{-1}$
p-OAcBuP[b]	CH_3	0.71±0.07	----	2400±100
32b	$CH_2CH{=}CH_2$	0.12±0.01	0.119±0.001[c]	405±15
33b	$(CH_2)_2CH{=}CH_2$	0.39±0.03	----	2360±80

[a]: degassed with diffusion pump. [b]: 4'-butyrylphenyl acetate.

[c]: plot of $1/\Phi_{II}$ versus ketone concentration had slope = 69±7 $\underline{M}^{-1}$ and intercept= 8.39±0.05

5. Maximised Quantum Yield

The quantum yield for the formation of 4'-acetylphenyl acetate from 4'-valerylphenyl acetate was maximised by addition of varying amounts of pyridine to 0.03 $\underline{M}$ degassed solutions of the ketone in benzene[14,16,21]. These data are reported in Table 3 and plotted in Figure 10. The discrepancy between Φ_{MAX} and Φ_{II} in methanol[21] can be possibly attributed to the low density of data points around the "true" Φ_{MAX} of the pyridine experiment.

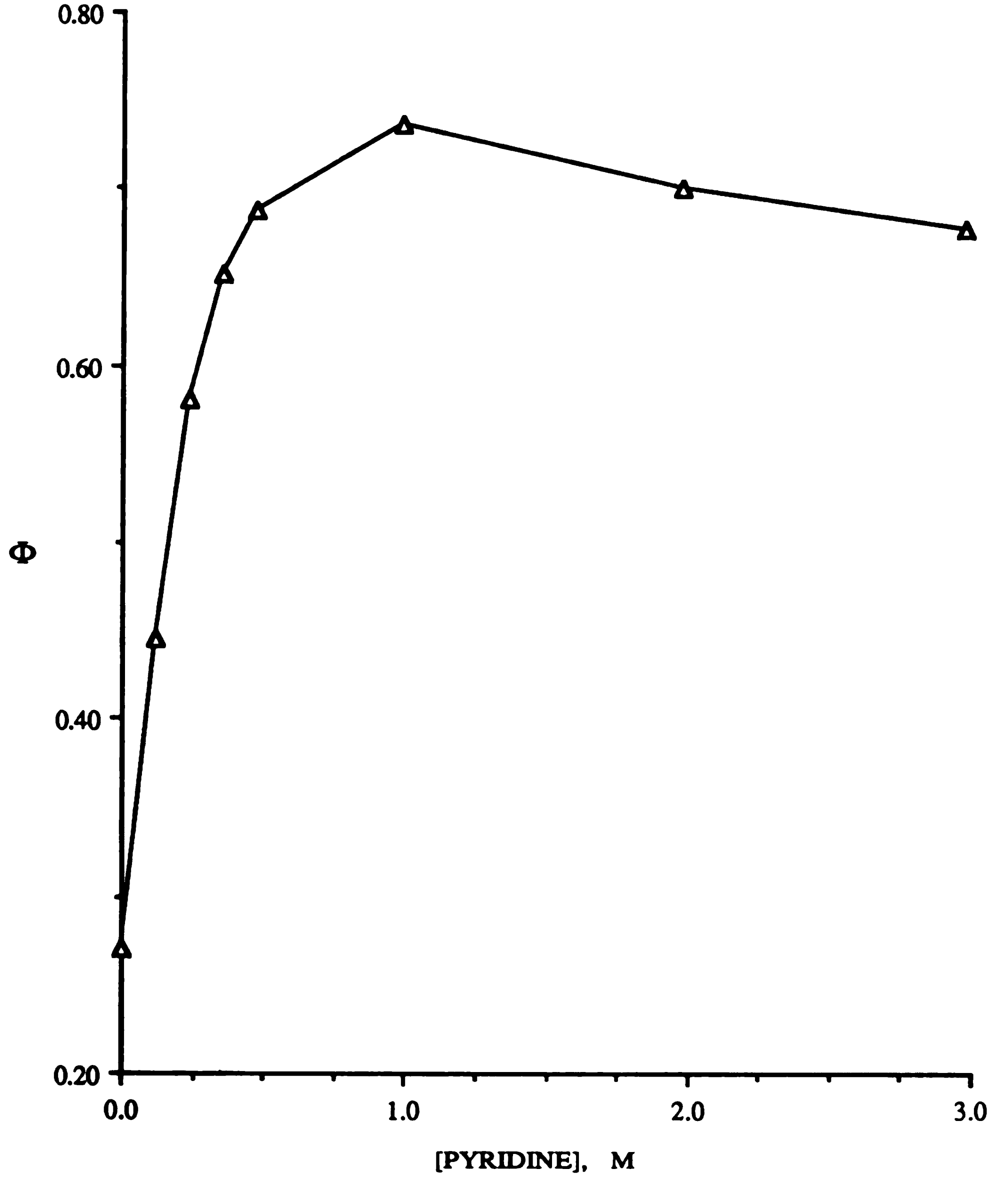


Figure 10. Dependence of Quantum Yield of Acetophenone Formation from 4'-Valerylphenyl Acetate on Concentration of Pyridine in Benzene.

Table 3. Quantum Yield- and Photokinetic- Parameters for Quenching of 4'-Valerylphenyl Acetate

Solvent	Quencher	Φ_{II}	Φ_{MAX}[a]	$k_q\tau$
benzene	DMHD	0.27±0.01	0.76	76±1
4:1-MeOH:phH	DMHD	0.85±0.03	----	190±20
4:1-MeOH:phH	me-crotonate	0.85±0.03	----	33±1

[a]: Φ_{MAX} measured as a function of pyridine concentration.

6. Crotonate Ester Quenching

The apparent instability of the 3-butenoate esters relative to their crotonate isomers necessitated correction for quenching of the 4'-butyrylphenyl 3-butenoate triplet state by its 4'-butyrylphenyl _trans_-crotonate isomer. The quenching ability of the crotonate moiety was assayed by comparison of Stern-Volmer slopes from separate experiments in which the Type II reaction of 4'-valerylphenyl acetate in 4:1-methanol: benzene was quenched by DMHD and methyl _trans_-crotonate (see Table 3 and Figure 11). The ratio of quenching rates was therefore equal to the quotient of the methyl crotonate to the DMHD Stern-Volmer slopes ie., k_q for me-crotonate, k_{cr}, was (33/190) x 100%= 17% of that of DMHD. The valerylphenyl- and not butyrylphenyl- acetate was used for this purpose because the lesser triplet lifetime of the former compound improved the precision of the consequent results. The associated rate constant, k_{cr}, and all other bimolecular quenching

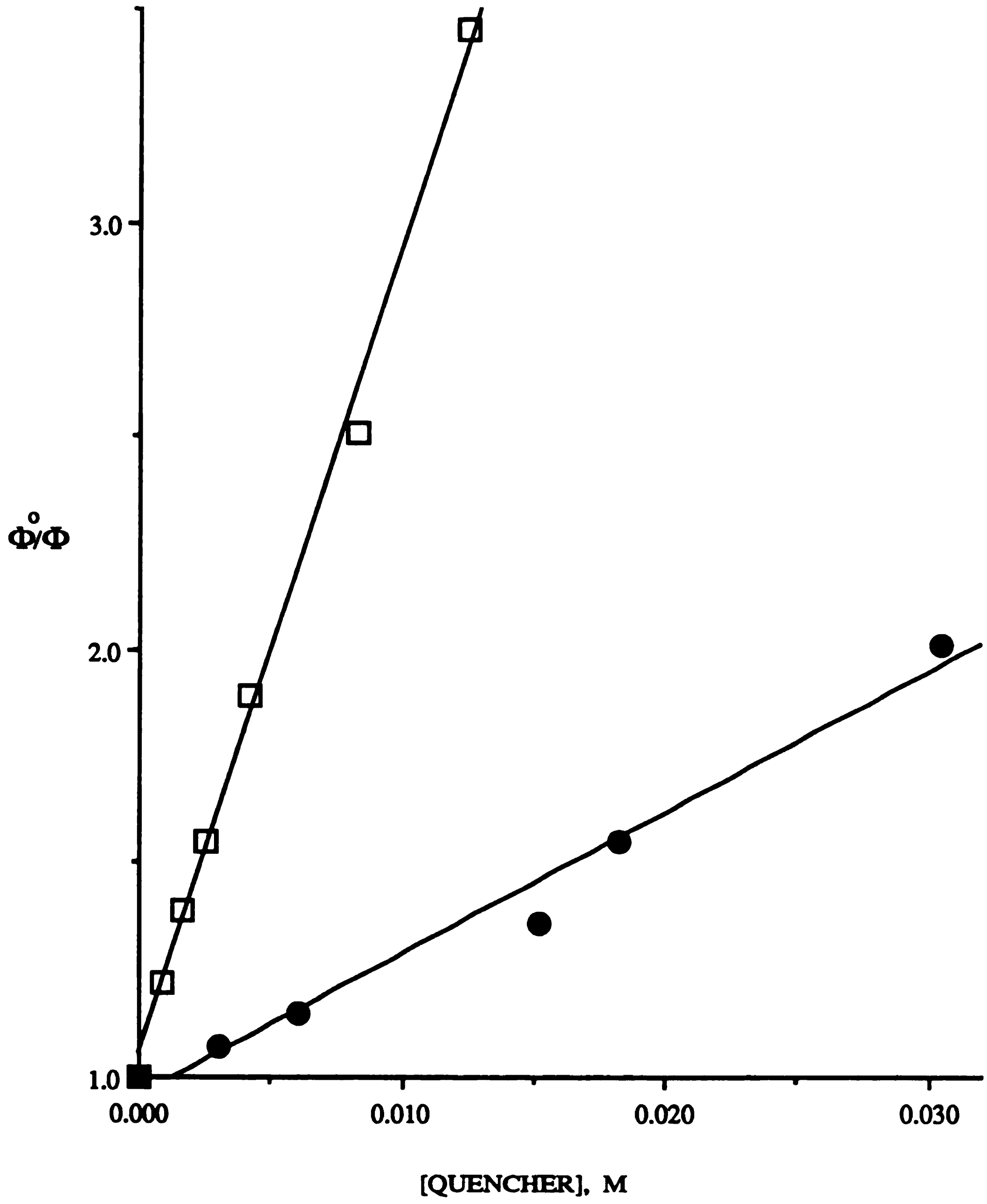


Figure 11. **Stern-Volmer Plot for Quenching of Acetophenone Formation from 4'-Valerylphenyl Acetate with Methyl Crotonate and 2,5-Dimethyl-2,4-Hexadiene in 4:1 - Methanol:Benzene.** Legend: 2,5-dimethyl-2,4-hexadiene: open square; methyl crotonate: closed circle.

processes reported in Table 8 (vide infra) are based on the assumptions (1) that k_q for methyl crotonate is the same as for 32b-crotonate and (2) that k_q of DMHD in 4:1-methanol:benzene is equal to that in pure methanol[21,98].

B. Preparative Irradiations

Generally, 0.055 to 0.003 M degassed and vacuum-sealed solutions of the appropriate acetophenone derivative in benzene-d_6 or methanol-d_4 containing traces of benzene-d_6 in 5 mm diameter pyrex NMR tubes were irradiated for varying times directly outside of a lamp surrounded by a pyrex filter. The 250 MHz ^{1}H NMR spectra of the solutions were recorded intermittantly and the results of their irradiation are reported in Table 4.

Table 4. Summary of Results of Irradiations of Acetophenones Through Pyrex Filter in 250 MHz Proton NMR Experiments.

Structure	[Ketone],M	Solvent	Result
29a	0.055	CD_3OD	1,2
29a	0.030	C_6D_6[a]	2
31a	0.044	CD_3OD	2
32a	0.030	CD_3OD	1
34a	0.0029	CD_3OD	2
35a	0.0030	CD_3OD	2

Key to results:

1: appearance of 2 upfield-shifted aromatic doublets noted.

2: insoluable material present at end of irradiation.

[a]: degassed by bubbling 10 min with Ar gas.

IV. DERIVED PHOTOKINETIC PARAMETERS

A. Triplet Lifetimes

The reciprocal triplet lifetimes of the valeryl and butyryl ketones were evaluated from the slopes of their Stern-Volmer plots (vide supra). In benzene[34], k_q was taken as 5.0×10^9 $\underline{M}^{-1}$ s^{-1}, while in 4:1-methanol:benzene the value for pure methanol[21], 7.5×10^9 s^{-1} was used. The reciprocal lifetimes are reported in Tables 5 - 7.

Table 5. Reciprocal Triplet Lifetimes of 4'-Valeryl Alkenyl Benzoate Esters

Photosubstrate	Alkenyl moiety	$10^{-7} \times \tau^{-1}$, s^{-1}
29b	$CH_2CH{=}CH_2$	9.1±0.5
31b	$(CH_2)_2CH{=}CH_2$	8.2±0.1

B. Rate Constants for Acetophenone Formation

The rate constants for formation of Type II cleavage products from the 4'-butyrylphenyl- and 4'-valerylphenyl esters were calculated from the expression $k_{II} = \Phi_{MAX}/\tau$, where Φ_{MAX} was taken as Φ_{II} in 4:1-methanol:benzene[19,21]. The rate constants are tabulated in Tables 6 and 7.

Table 6. Rate Constants for Acetophenone Formation and Reciprocal Triplet Lifetimes of 4′-Butyrylphenyl Alkenoate Esters

Photosubstrate	Acid Residue	$10^{-6} \times \tau^{-1}, s^{-1}$	$10^{-6} \times k_{II}, s^{-1}$
p-OAcBuP	CH_3	3.1±0.1	2.2±0.3
32b	$CH_2CH{=}CH_2$	18.5±0.7[a]	2.2±0.3
33b	$(CH_2)_2CH{=}CH_2$	3.2±0.1	1.2±0.1[b]

[a]: uncorrected for quenching by crotonate isomer and ground state ketone. [b]: see Discussion.

Table 7. Rate Constants for Acetophenone Formation and Reciprocal Triplet Lifetimes of 4′-Acylphenyl Acetate Esters

Ketone	Solvent	$10^{-7} \times \tau^{-1}, s^{-1}$	$10^{-7} \times k_{II}, s^{-1}$
p-OAcVP[a]	benzene	6.58±0.09	5.6
p-OAcVP	methanol:benzene	3.5±0.4	3.0
p-OAcBuP	methanol:benzene	0.31±0.01	0.22

[a]: 4′-valerylphenyl acetate

C. 4'-Butyrylphenyl 3-Butenoate Parameters

1. Bimolecular- and Intrinsic- Decay

The plot of $1/\Phi_{II}$ versus concentration of 32b in Figure 9 was reasonably linear and was analysed according to Equation 13 [13,53a,99].

$$1/\Phi = 1/P(1 + k_d/k_r) + 1/P(k_{inter}[K]/k_r) \qquad (13)$$

Here, P stood for the fraction of acetophenone photoproducts, k_d was the rate constant for the sum of unimolecular decay processes leading back to ground state photosubstrate and k_{inter} was the bimolecular rate constant for quenching of the triplet state by both the α,β- and β,γ-unsaturated isomers of 32b. Thus, the line had a slope equal to $k_{inter}/(Pk_r)$ and an intercept of $1/P(1 + k_d/k_r)$. Taking $Pk_r = k_{II}$, the experimentally measured rate constant for formation of acetophenone 32a and estimating the value of P for Type II reaction of butyrophenone in alcoholic medium from the literature data[10c] as 0.92, therefore allowed evaluation of k_{inter} and k_d. These values can be found in Table 8.

2. Intramolecular Quenching Rate Constant

The rate constant for intramolecular quenching by the tethered 3-butenoate residue of 32b, k_{CT} was calculated as described in Equation 14 [53a], where k_d^{model} was the rate constant for the sum of the

$$k_{CT} = k_d - k_d^{model} \qquad (14)$$

unimolecular decay processes of 4'-butyrylphenyl acetate leading back to the ground state photosubstrate. The k_d^{model} was determined as $1/\tau^{model} - k_{II}^{model}/P$, where P was defined as before. This value, and that of k_{CT} are reported in Table 8.

3. Intramolecular Quenching Quantum Efficiency

The calculation of the quantum yield for intramolecular quenching, Φ_{CT} required knowledge of the triplet lifetime of 32b in the absence of intermolecular quenching, τ_0. This quantity is given in Equation 15,

$$1/\tau_0 = (\Phi_{0.03}/\Phi_0) \cdot 1/\tau_{0.03} \qquad (15)$$

where $\Phi_{0.03}$ and $\Phi_0 = \Phi_{LIM}$ were the quantum yields of acetophenone formation at 0.03 M and 0 M (extrapolated) photosubstrate concentrations, taken from the line equation of Figure 9, and $\tau_{0.03}$ was the triplet lifetime for 0.03 M photosubstrate, taken from the Stern-Volmer experiments[53a]. This value and that of Φ_{CT}, determined as $k_{CT} \cdot \tau_0$, are both found in Table 8.

4. Ground State Quenching

Knowledge of k_{inter} from the reciprocal quantum yield study, k_{cr} from the methyl crotonate quenching experiment and the fractions of 3-butenoate and trans-crotonate isomers of 32b in the photolysis solutions, χ_i, through HPLC enabled estimation of the rate constant for self-quenching by the ground state photosubstrate, k_{sq} as shown in Equation 16[53a]. Table 8 summarises k_{sq} and the unimolecular quenching rate increments contributed by each isomer at the 0.03 M level.

$$k_{inter} = k_{cr} \cdot \chi_{cr} + k_{sq} \cdot \chi_K \qquad (16)$$

Table 8. Miscellaneous Parameters from 4'-Butyrylphenyl 3-Butenoate Experiments

Parameter	10^{-7} x Value
k_{inter}	$15 \pm 5\ \underline{M}^{-1} s^{-1}$
k_d	$1.5 \pm 0.3\ s^{-1}$
k_d^{model}	$0.24 \pm 0.03\ s^{-1}$
k_{CT}	$1.3 \pm 0.3\ s^{-1}$
$1/\tau_0$	$1.5 \pm 0.2\ s^{-1}$
$1/\tau_{0.03}$	$1.85 \pm 0.07\ s^{-1}$
k_{cr}	$130 \pm 30\ \underline{M}^{-1} s^{-1}$
k_{sq}	$10 \pm 4\ \underline{M}^{-1} s^{-1}$
$k_{cr}[\underline{32b}\text{-crotonate}]$	$0.16\ s^{-1}$
$k_{sq}[\underline{32b}]$	$0.29\ s^{-1}$
Φ_{CT}	0.85 ± 0.32

V. TRIPLET ENERGIES

The triplet energies of 4'-valerylphenyl acetate in 2-methyltetrahydrofuran- and 5:1-methanol:ethanol- glasses upon 313 nm excitation at 77°K were calculated from their 0,0 phosphorescent bands and are reported in Table 9.

Table 9. Triplet Energies of 4'-Valerylphenyl Acetate in Different Solvent Glasses at 77°K

Solvent Glass	E_T, kcal/mol
2-methyltetrahydrofuran	72.6
5:1-methanol:ethanol	72.0

VI. MOLECULAR MECHANICS CALCULATIONS

The MMX87 molecular mechanics program was used to roughly model the stability of conformations of ground state 4'-acetyl allyl benzoate and 4'-acetylphenyl 3-butenoate wherein the olefin tether was proximate to the phenyl ring. This was accomplished by systematically varying the carbon-oxygen ester dihedral angle β to the phenyl ring and allowing the program to select the conformations which were otherwise of least energy. The stability of the conformers thus generated was compared to those produced by the program without dihedral restraints.

The thermodynamic results were given as STRAIN ENERGIES, the calculated difference in heats of formation between the molecule itself and a hypothetically totally strain-free molecule of the same constitution in a vacuum[100]. These calculations were approximate at best and should only be used to compare the energies and intramolecular distances within different conformations of the same molecule. The STRAIN ENERGY of the most stable conformation as well as of a function of β along with analytical descriptions of tether geometry are tabulated below in Tables 9 and 10.

Table 10. Dependence of STRAIN ENERGIES, Intramolecular Aromatic - Olefin Distances and Tether Geometry on Ester Dihedral Angle β to the Phenyl Ring in 4'-Acetyl Allyl Benzoate[a]

β, °	STRAIN ENERGY, kcal/mol	α, °	γ, °	Distance, Å[b]
179[c]	14.338			4.78-5.82
180	14.324	3.56	178.4	4.78-5.82
170	14.652	8.73	173.25	4.78-5.79
160	16.197	18.23	147.85	4.77-5.81
150	17.560	22.83	145.94	4.78-5.80
140	19.163	22.29	147.00	4.79-5.77
130	20.969	20.24	148.38	4.79-5.73
120	22.957	18.84	149.42	4.79-5.71
110	24.562	18.11	149.92	4.48-5.69
100	25.713	17.61	150.25	4.76-5.67
90	26.091	17.48	132.66	4.73-5.65
80	26.873	17.80	151.16	4.69-5.62
70	26.393	18.84	151.44	4.64-5.59
60	25.116	21.56	149.77	4.60-5.49
50	25.913	-2.80	-138.49	4.60-5.49
40	24.318	-57.56	-178.23	4.52-5.34
30	22.867	-59.80	-175.05	4.47-5.26
20	21.713	-59.52	-169.63	4.43-5.22
10	20.861	-58.32	-164.93	4.41-5.19
0	20.412	-55.42	-160.34	4.40-5.19

[a]: **see Figure 12 for definition of angles** α, β **and** γ. [b]: **distances between C(2) - C(3) of the allyl group and the carboxylic aromatic carbon.** [c]: **calculated without dihedral driver.**

Table 11. Dependence of STRAIN ENERGIES, Intramolecular Aromatic-Olefin Distances and Tether Geometry on Ester Dihedral Angle β to the Phenyl Ring in 4'-Acetylphenyl 3-Butenoate[a].

β, °	STRAIN ENERGY, kcal/mol	α, °	γ, °	Distance, Å [b]
179[c]	18.316	-55.11	-97.63	4.57-5.73
180	18.337	-54.20	-95.06	4.46-5.71
170	18.529	-54.12	-93.39	4.48-5.62
160	19.168	-54.53	-92.52	4.39-5.53
150	20.170	-55.11	-91.40	4.29-5.43
140	21.455	-55.14	-91.43	4.19-5.34
130	23.087	-55.42	-91.34	4.09-5.24
120	25.205	-55.98	-89.27	4.01-5.15
110	27.808	-54.76	-87.89	3.95-4.97
100	29.446	-84.56	-78.15	3.65-3.92
90	29.775	-92.67	-70.61	3.47-3.69
80	29.829	-97.30	-65.60	3.30-3.50
70	29.454	-100.00	-62.95	3.17-3.46
60	29.612	-102.70	-59.96	3.05-3.46
50	27.462	-118.91	-37.54	2.94-3.72
40	23.149	-132.52	64.07	3.48-3.73
30	21.512	-127.74	68.79	3.48-3.72
20	20.437	-122.53	72.55	3.47-3.69
10	19.771	-112.91	76.79	3.46-3.68
0	19.566	-104.88	76.84	3.61-3.69

[a]: see Figure 13 for definition of angles α, β and γ. [b]: distances are those between the butenoate C(3) - C(4) and the phenolic carbon. [c]: calculated without dihedral driver.

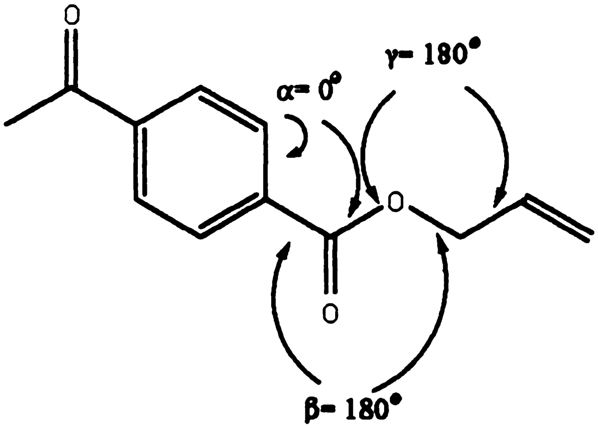


Figure 12. Conformation of 4'-Acetyl Allyl Benzoate Defined for Dihedral Angles α= 0°, β= 180° and γ= 180°.

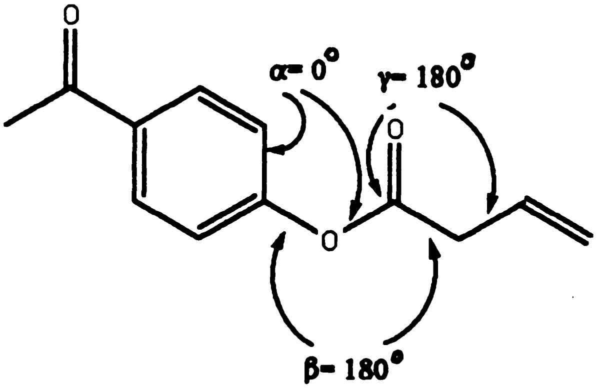


Figure 13. Conformation of 4'-Acetylphenyl 3-Butenoate Defined for Dihedral Angles α= 0°, β= 180° and γ= 180°.

DISCUSSION

I. ACYL ALKENYL BENZOATE ESTERS

A. Photokinetic Parameters

Comparison of $1/\tau$ and Φ_{II} of 29b and 31b to the values found by Siebert for p-carbomethoxyvalerophenone[50] indicated that no intramolecular quenching of their π,π^* triplet excited states occurred[53], well within experimental error. This seems to have been true also for the prenyl ester 30b, although its Φ_{II} was inexplicably slightly higher than those of the other three esters.

B. Preparative Irradiations

The irradiations of 29a, 31a, 34a and 35a failed to show the presence of any peaks in their ^{1}H NMR spectra which could have arisen from products of photocycloaddition of the olefin onto the aromatic ring.

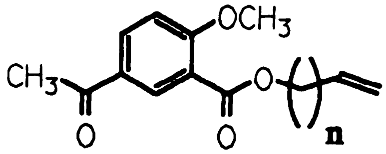
C. Lack of π,π^* Photoreactivity

The failure of these compounds to show any intramolecular interaction between the triplet state ketone and the olefinic tethers can probably be at least partially traced to the strain which would have been effected by the sp^2-geometry of their ester linkages in a C.T.-quenching transition state.

Simple molecular models of 4'-acetyl allyl benzoate showed that in order to gain access to *any* conformations favourable to quenching, the carbonyl carbon - alkyl oxygen bond must be rotated out of the plane defined by the lowest energy trans-coplanar conjugated benzoate array. The molecular mechanics calculations suggested the energy barrier for this motion could be prohibitively high, for example, ca. 13 kcal/mol for the conformation in which this bond is perpendicular to the aromatic ring. Also, in none of the resulting energy minimised conformations did the calculated distance between the olefin and the aromatic carbon bearing the carboxylate moiety fall below 4.6 Å, or 0.38 Å less than in the trans- coplanar conformation (see Table 10).

In agreement with the strain hypothesis was also Winnik's observation[49] that, in the ω-alkenyl p-benzoylbenzoate ester series, the shortest tether where the olefin could touch the aromatic ring without breaking the trans coplanar phenyl-ester conformation corresponded to 5-hexenoate.

Further support for this hypothesis can be garnered by the absence of photoreactivity from the 5'-acetyl-2'-methoxy alkenyl benzoate esters, 34a and 35a. Significantly, photocycloaddition should have



34a, n= 1

35a, n= 2

been favoured in these compounds on electronic grounds. This is because the _para_ orientation of the acetyl- and methoxy- moieties is thought to give a π,π^* triplet state with much charge-transfer character[21], possibly an essential element in the photocycloaddition mechanism[53a].

In comparison to the facile intramolecular quenching of Siebert's analogously tethered tertiary amino valeryl esters[50], it is apparent that the ca. 2 eV higher ionisation potentials of terminal n-alkyl olefins than for tertiary amines[52] dictate alot more stringent spatial quenching requirements from the former.

However, none of the foregoing excludes the lack of sufficiently strong charge transfer character from the 4'-acyl benzoate chromophore triplet state, relative to the intrinsic quenching ablilities of alkenes[41], as an additional culprit for the absence of intramolecular phenomena.

II. 4'-BUTYRYLPHENYL ALKENOATE ESTERS

A. Intramolecular Quenching

The photokinetic- and quantum yield data of 4'-butyrylphenyl 3-butenoate but not 4'-butyrylphenyl 4-pentenoate were indicative of quenching of the 4'-butyrylphenyl chromophore's π,π^* triplet state[50,53]. The intramolecular nature of this phenomenon was proven by the study of reciprocal quantum yield versus photosubstrate concentration and the corrections which were then allowed for additional bimolecular quenching[50,53a]. That k_{CT} from the mildly electron deficient 3-butenoate residue was even lower than for the acylphenyl alkenyl ethers[53a] suggested that quenching here proceeded through a C.T.- and not E.T.- mitigated mechanism[29,30]. This is also precedented by the known preference for C.T. quenching of alkylphenyl ketones by olefines[37].

B. Quenching Geometry

The magnitude of the k_{CT} value observed for the 4'-butyrylphenyl 3-butenoate was much less than those of Nahm's alkenyl ethers[53] and no compareable photoproducts were formed. Nevertheless, Φ_{CT} showed this process to be relatively efficient, a fact which can be rationalised through examination of the geometrical requirements for intramolecular quenching.

Molecular models of 4'-acetylphenyl 3-butenoate showed that motion of the ester bond β to the phenyl ring, ie. the phenyl oxygen-carbonyl carbon bond, is again necessary for close approach of the olefin to the phenolic aromatic carbon. This observation was supported by the molecular mechanics studies on the energetics of and olefin-aromatic ring proximities available to 4'-acetylphenyl 3-butenoate upon rotation of this bond. In the 10° (from <u>cis</u> coplanar) to 90° conformers, the distance between the butenoate C3 position and the phenolic carbon was calculated to be between 2.94 and 3.47 Å, or 1.10 to 1.63 Å less than in the most stable, <u>trans</u> coplanar conformation. As well, the STRAIN ENERGIES of the 10° to 40° rotamers were only 1.5 to 4.8 kcal/mol higher than the <u>trans</u> coplanar conformer, while the distance was still ca. 3.47 Å (see Table 11).

The likelyhood of C.T. interactions occurring from <u>gauche</u> conformations of <u>32b</u> is supported by Karabatsos' ^{13}C NMR- based measurements on the conformational preferences about the β bond of phenyl acetate[101]. His experiments indicated a 47% <u>gauche</u> - 53% <u>trans</u> population at 0°C (ΔH^{o}= ca. 0.6 - 1.5 kcal/mol). Analogy to the rotational preferences of the 3-butenoate ester is imperfect, however. Although the vinyl group of the butenoate residue would not be expected to sterically interfere[102] with the rotating element, the presence of the 4'-acyl group on the aromatic ring should stabilise the <u>trans</u>-coplanar conformation through ground state configurational effects.

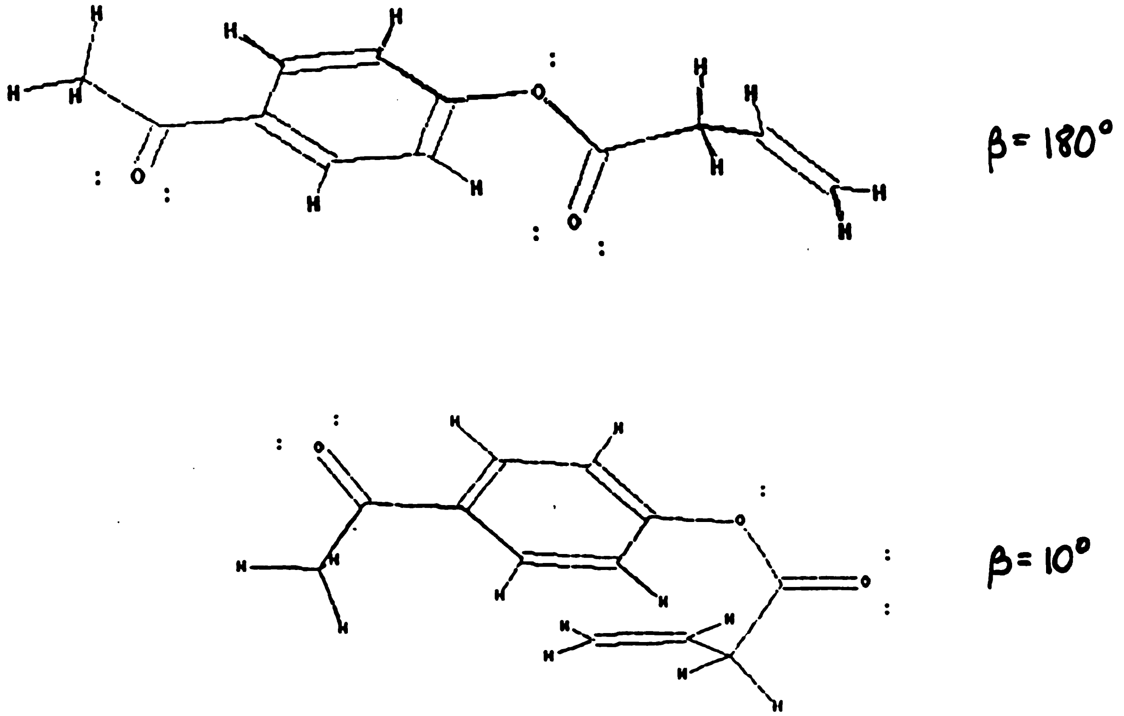


Figure 14. **Minimised Energy Molecular Mechanics Geometries of 4'-Acetylphenyl 3-Butenoate For Phenyl Oxygen - Ester Carbonyl Carbon Bond <u>trans</u> Coplanar- and 170°-from-<u>trans</u> Coplanar- Conformations.**

Thus, intramolecular C.T. quenching is geometrically understandable in <u>32b</u>. The apparent lack of photocycloadducts here may have been a reflection of the strain of closure of the presumed 1,4-biradical resulting from breakdown of the C.T. complex[57c]. The combination of lack of strong charge transfer character in the 4'-butyrylphenyl alkenoate excited state and the presumeably high oxidation potential of the 3-butenoate residue may have also been a factor in this.

The lack of intramolecular C.T. quenching which the reciprocal lifetime of 4'-butyrylphenyl 4-pentenoate indicated for that compound is hardly surprising. The 3-butenoate experiments showed that the strength of this type of C.T. interaction was very weak, which in combination with the known propensity toward 3-atom tether interactions in intramolecular olefin C.T.[47,53,57b], would have predicted an insignifcant contribution from intramolecular quenching to the reciprocal triplet lifetime of 33b. The slight disagreement between the quantum yield- and $1/\tau$- values for 33b, relative to those of the acetate- and butenoate- esters bears mention, however. The obvious culprit here was imprecise actinometry, since the acetate- and butenoate- data were mutually consistent, and the pentenoate Stern-Volmer data were internally consistent and employed reasonable GC -response factors and -analysis profiles.

C. Experimental Complications

1. Instability of 3-Butenoate Esters

The instability of 32 in solution could probaly be traced to the basic nature of the photolysis glasswares' surfaces, further exacerbated by the routine cleaning of the glassware with a basic detergent (see "Experimental"). Thus, the surfaces provided an isomerisation medium, in analogy to the rapid rearrangement of alkyl 3-butenoates to mixtures of their cis and trans crotonate isomers in the presence of metal alkoxides[103].

The instability of the 3-butenoate esters in a 150° GC column was also not unexpected, since 3-butenoic acid is thought to exist in equilibrium with its crotonate isomers at temperatures above 100°C[104].

Thus, only HPLC could be used in the analysis of the post-photolysis solutions.

2. 4'-Acetylphenyl 3-Butenoate Analysis Conditions

Significantly, two different reverse phase HPLC systems were used for measurement of concentrations of photoproduct 32a; the conditions and qualities of the consequent analysis profiles were not equivalent (see "Experimental" and "Appendix"). The Stern-Volmer experiments were analysed on the 25 cm ODS octyl column, eluting with methanol - water mixtures. Photoproduct and internal standard (ethyl benzoate) eluted at 7.2 and 13.0 min, respectively. This system was the one of choice; unfortunately the column suffered a sudden, severe loss of plate numbers after those experiments had been completed. Thus, the reciprocal quantum yield study had to be conducted on the 25 cm phenyl reverse phase column, eluting with acetonitrile - water mixtures. The photoproduct and internal standard (^{n}octyl benzoate) eluted at 15.9 and 22.6 min; however an unidentified impurity which increased in concentration with the concentration of 32b eluted close to the standard at 22.1 min.

The quantum yields which were determined from those latter measurements were consequently thought to be slighly lower than those which could have been achived on the ODS octyl column. For example, quantum yields at the 0.03 M photosubstrate level from the ODS-octyl and phenyl columns were 0.12±0.01 and 0.097±0.001, respectively. Although the relative difference between these two measurements is small, the reciprocal quantum yield study was designed to measure small differences in quantum yields as a function of concentration of 32b. This discrepancy is perhaps best demonstratd through Table 2, where Φ_{II} (from the Stern-Volmer experiments) is actually the same as Φ_{LIM} (extrapolated from the reciprocal quantum yield study), in opposition to the trend of decreasing quantum yields with increasing photosubstrate concentration. However, since this error was more pronounced at higher concentrations of photosustrate, it is likely that its effect was significantly greater on the *slope* than on the *intercept* of the plot of Figure 9. Therefore, some minor (ca.10%) underestimation of the actual values for only k_{inter} and $1/\tau_0$ (cf. Equation 13) is expected; hence k_{sq} should really be somewhat higher and Φ_{CT} ca. 10% lower, than the values reported in Table 8.

III. 4'-ACYLPHENYL ACETATE ESTERS

A. Lowest Triplet State

The current data appear to describe 4'-acylphenyl acetate ketones in terms of having weak π,π^* lowest triplet states. Photochemical evidence includes a triplet lifetime and quantum yield for the valerylphenyl ester in benzene compareable to those of known π,π^* lowest triplet valerophenones having conjugatively weakly donating substituents[21,23], as well as the intramolecular C.T. quenching studies[50,53]. The phosphorescence spectrum of the valeryl ester featured a relatively amorphous hump in both 2-methyltetrahydrofuran and 5:1 - methanol:ethanol glasses, characteristic of a π,π^* lowest triplet state[104]. No emission from an n,π^* state was seen in either glass. This qualitatively agrees with Pitts' earlier assignment of the lowest triplet state 4'-acylphenyl acetate chromophore[17]. The small red shift of the 0,0 band in going to the alcohol mixture, corresponding to ca. 0.6 kcal/mol stabilisation, is also similar in magnitude to that of the p-carbomethyoxy- and -cyano-valerophenones[23].

However, the weakness of this energetic preference is revealed by the great rise in quantum yield of the valerylphenyl ester upon changing from benzene to methanol:benzene. When the expected extent of unassayed cyclobutanol photoproducts are considered, ca. 8% [10c], the quantum yield for formation of all hydrogen-abstraction derived products probaly approaches unity. This is similar to the behaviour of n,π^* lowest triplet ketones[21,106] and those with isoenergetic triplets[21]. It also contrasts ketones with known strongly π,π^* lowest triplet states, like para-methoxyvalerophenone[21].

The observed rate constants for formation of cleavage products are the first known for the acetoxy substituent. The overall accuracy of the 4'-butyrylphenyl- and 4'-valerylphenyl- acetate data is attested to by the ratio of rates in 4:1-methanol:benzene, ca. 13. This is within the range of ratios of other $^3n,\pi^*$- and $^3\pi,\pi^*$- lowest triplet butyrophenone and valerophenone systems[21], demonstrating the greater rates of hydrogen abstraction by alkoxy-type radicals from secondary than from primary centers[107].

The current rate measurements also support the previous conclusions on relative triplet energetics. The rate constant for acetophenone formation from 4'-valerylphenyl acetate drops by 60% upon changing from benzene to 4:1 - methanol:benzene; quantitatively, the same trend is evident for the simple valerophenone - benzene/methanol (pure) system[21] (k_{pOAcVP}/k_{VP}= 0.44). The lower rate constant for the acetyloxy ketone is undoubtedly a consequence of its π,π^* lowest triplet state[21]. However, alot more drastic drop in reactivity was seen from more strongly π,π^* lowest triplet ketones[21]. The influence of methanol on the relative energy levels of the reactive n,π^* triplet states for valerophenone and 4'-acylphenyl acetates would therefore seem to be identical.

Although this current study did not directly measure the n,π^* and π,π^* triplet energies of the 4'-acylphenyl acetates at room temperature, the energy gap between them could be estimated as follows: Since $1/\tau \approx k_{II}$ for 4'-valerylphenyl acetate[23], the σ_I inductive substituent for the 4'-acetyloxy group, 0.38[108] could be used in a plot of $\log(k^n{}_x/k_o)$ (k_o= cleavage rate constant for simple valerophenone in benzene) versus σ for n,π^* lowest triplet valerophenones substituted with inductively withdrawing groups[25] to extrapolate a value of the anticipated rate constant for acetophenone formation in the absence of the resonance effects which resulted in the observed π,π^*-type reactivity, $k^n{}_{pOAcVP} = 2.2 \times 10^8\ s^{-1}$. This value and k_{pOAcVP} were then substituted into Equation 1 (see page 10) to give the fractional populations of the two states. From $\chi_{n,\pi}$= 0.25, Equation 2 was employed to obtain ΔE= 0.65 kcal/mol. Since ΔE for 4'-valerylbenzonitrile[25] is 0.67 kcal/mol, ($k_{II} = 2.9 \times 10^7\ s^{-1}$), the electronic effects of the 4'-acetyloxy group on the relative ordering of the $^3n,\pi^*$ and $^3\pi,\pi^*$ energies would seem to be similar to those of the cyano group.

At this point it was tempting to estimate $E_{n,\pi}$ for the current photosubstrates in benzene at room temperature as E_T (in 2-methyltetrahydrofuran at 77°K) + ΔE and then go on to use $E_{n,\pi}$ for valerophenone in alcoholic glass and the conclusion that the difference in $E_{n,\pi}$ between the two compounds was solvent independent to estimate $E_{n,\pi}$ for the current case in 4:1 - methanol:benzene. Neither of these lines of logic are valid however, since triplet energies in low temperature solvent glasses are known to differ from those for room temperature solution[25,29]. Instead, Table 12 compares the phosphorescence energies of 4'-valerylphenyl acetate to the estimated room temperature triplet energies of 4'-valerylbenzonitrile[23] and valerophenone[25].

Table 12. **Comparison of Phosphorescence π,π^* Triplet Energies of 4'-Valerylphenyl Acetate to n,π^* and π,π^* Triplet Energies of Several Aryl Alkyl Ketones in Non-Polar Solvent**

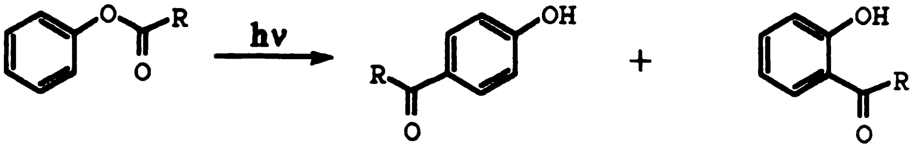
Ketone	$E_{n,\pi}$, kcal/mol	$E_{\pi,\pi}$, kcal/mol
pOAcVP[a]	----	72.6 (72.0)[b]
pCNVP[c]	71.2	69.3
VP[d]	73.4	75.5

[a]: phosphorescence energies determined from 0,0 lowest energy bands at 77°K. [b]: measured in 5:1-methanol:ethanol at 77°K.

[c]: 4'-valerylbenzonitrile. [d]: valerophenone.

B. Absence of [1,3] - Type Migration

This study also had relevance on the mechanism of the photo-Fries rearrangement[109]. Although much evidence indicates that it generally proceeds through a singlet, and not triplet[110] state, this has not been



unequivocably proven. Indeed, 4'-acetylphenyl benzoate shows a ca. 0.11 quantum yield of photosubstrate disappearance[109b]. Likewise, in spite of its apparent insensitivity to triplet state -sensitisers and -quenchers, the reactivity of 1-naphthyl acetate has been suggested, in principle to stem from either state[109a] because of its 0.29 singlet -> triplet intersystem crossing quantum yield[2]. The [1,3] rearrangement of β,γ-unsaturated ketones has also been proposed to occur from an upper triplet state[111]. Consequently, the 4'-acylphenyl acetate photosubstrates were especially suited to further probing this question.

The lack of π,π^* (or other triplet state) -mitigated photo-Fries rearrangement is perhaps best demonstrated by the approximately unitary quantum yield for Type II cleavage of 4'-valerylphenyl acetate. This point is further emphasised by the fact that polar solvents are known to favour the formation of intramolecular photo-Fries type products[109a]- the increased Type II quantum yield for this ketone upon changing from benzene to 4:1-methanol:benzene is contrary to this expectation. Also in opposition is the known enhancement in polar solvents of triplet state reactivity toward homolytic bond cleavage[112].

As well, in both of the acetate ester post-photolysis solutions the only high retention time peaks visible on the gas chromatographic traces were attributed to photosubstrate, photoproduct, internal standard and two small, broad, closely eluting peaks presumeably[10a] from cyclobutanols. This is significant, because rate constants for dissociation of singlet excited polyatomic molecules[113] have been estimated to be at least 10^{12} s^{-1}, ca. 10^{2} s^{-1} faster than that of singlet -> triplet intersystem crossing for phenyl alkyl ketones[2].

Thus, even any possibility of singlet photo-Fries reactivity from the current chromophores appears to be ruled out.

IV. Conclusion

A. Summary

This Work showed that limited intramolecular C.T. quenching of the π,π^* triplet state through the aromatic ring of 4'-acylphenyl ω-alkenoate, but not 4'-acyl ω-alkenyl benzoate esters, is possible. This difference stems from the propensity toward physical contact possible between the tethered olefin and the aromatic ring of the chromophore and apparently not the extent of charge transfer polarisation intrinsic to the lowest triplet state of each. The photokinetic- and spectroscopic- properties of the 4'-acylphenyl acetate chromophores parallel those of other phenyl ^{n}alkyl ketones which posess the π,π^* lowest energy triplet configuration, but suggest that this electronic configuration is only slightly preferred over the n,π^* one. Together these conclusions imply that intramolecular C.T. quenching through the aromatic ring of weakly dominant π,π^* triplets by tethered olefines is possible.

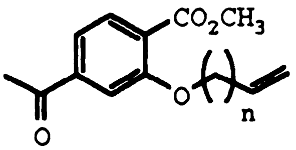
B. Reccomendations

There are many phenyl alkyl ketone-based, aromatic-tethered photosubstrates which, *ad hoc*, could give rise to C.T. quenching and/or intramolecular cycloaddition products. The esters studied in this Thesis give more realistic estimates of which cases might be fruitfully explored. The compounds described below are ordered in their pertinence to this Work and the ease of their preparation. As well, molecular mechanics calculations might be suggested to evaluate geometrical considerations before a given compound is studied.

Other 4'-Acyl Alkenyl Benzoates. Winnik's conclusions on the relative abilities of benzoate-tethered ω-alkenes to contact the aromatic ring as a function of chain length suggest that the Type II kinetics of 4'-valeryl benzoates having 5-hexenyl and 6-heptenyl ester tethers be examined. Although photocyloproducts might not be formed, insight on the susceptibility of the 4'-acyl benzoate chromophore ($E_{n,\pi} - E_{\pi,\pi} = 0.3$ kcal/mol)[23] toward intramolecular quenching by alkenes could be obtained.

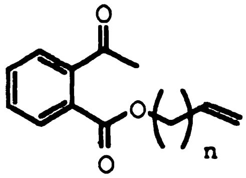
2'-Alkenyl-4'-Acetyl Methyl Benzoates. The alter ego of the 5'-acetyl-2'-methoxy alkenyl benzoates, the compounds 36 would combine the favourable geometry of the 4'-acylphenyl alkenyl ethers with the electronic configuration of the 4'-acyl benzoates. The isolation of [2+2] photocycloadducts from their irradiation would confirm the proposed geometrical limitations on C.T. quenching.

Ortho-Acyl Benzoate Esters. The π,π^* triplet state of o-carbomethoxyvalerophenone is estimated to be stabilised over the n,π^* one by ca. 0.7 kcal/mol more than the para isomer[23], suggesting that compounds 37 might show greater promise of C.T. quenching of the π,π^* triplet state respectively.



36

n= 2, 3

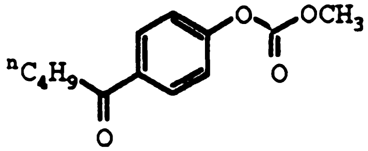


37

R= CH_3, $^nC_4H_9$

n= 1, 2

4'-Butyrylphenyl Methyl- and Vinyl- Carbonates. The presence of two oxygen atoms to reduce the electron deficiency of the tether carbonyl of 38 should improve the preference for the π,π^* lowest triplet state through charge transfer polarisation. Whether this would result in C.T. quenching and photocycloaddition in 39 would depend on the preference of the vinyl carbonate for a trans-coplanar conformation.



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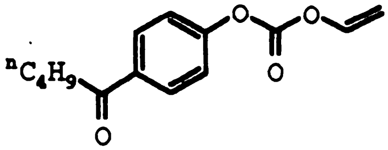
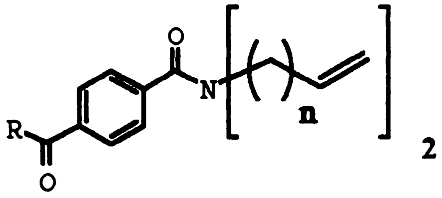


39

4'-Acyl N,N-Dialkenyl Benzamides. The trans-coplanar lowest energy conformation of the 4'-acyl alkenyl benzoates[102] does not favour contact between the olefin and the aromatic ring. This problem would be alieviated in the 4'-acyl dialkenyl benzamide series, 40. The sp^2

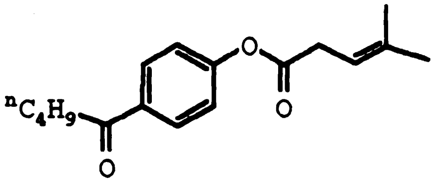
geometry around the amide nitrogen[114] would force one of the tethers to be proximate to the ring.

4'-Butyrylphenyl 4-Methyl-3-Pentenoate. The photokinetics of 41 should demonstrate greater C.T. quenching than of the 3-butenoate ester, by virtue of the greater electron-donating ability of the more highly substituted tether[37,53a]. Photocycloadducts may also be possible.



40

R= CH_3, $^nC_4H_9$
n= 1, 2



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EXPERIMENTAL

I. PURIFICATION AND PREPARATION OF CHEMICALS

A. Solvents and Additives

Benzene. Baker Reagent Grade benzene was purified in 4 l lots by stirring repeatedly for periods of ca. 1 day with 150 ml concentrated H_2SO_4 untill no discolouration was apparent in the acid layer. It was then washed 3 times each successively, with water, saturated $NaHCO_3$ solution, water and saturated NaCl solution. After drying over $MgSO_4$, followed by refluxing over P_2O_5, it was distilled through a 0.9 m heated glass column packed with glass helicies at a rate of ca. 100 ml/h. The central cut, ca. 70% of the total distillate volume, was collected[81].

Methanol. To 4 l of Baker Reagent Grade methanol was added ca. 10 g of freshly cut sodium metal. After refluxing overnight, it was fractionated through a 30 cm Vigreux column. The central cut, ca. 60% of the total distillate volume, was collected.

Pyridine. A 500 ml volume of Fisher Reagent Grade pyridine was refluxed for 2 days over 7 g BaO and fractionally distilled twice through a 30 cm column packed with copper mesh. In each case, the central 70% of the total distillate volume was collected.

Reverse Phase HPLC Solvents.

a) Ultraviolett-HPLC grade methanol and acetonitrile were passed through a 0.45 μ mesh Nylon-66 filter prior to use.

b) Distilled water was refluxed overnight as a 0.012 $\underline{M}$ NaOH - 0.0012 $\underline{M}$ $KMnO_4$ solution and fractionated through a 1.5 m glass Vigreux column. The central 50% of the total volume was collected and immediately stored as an 10% -acetonitrile or -methanol solution.

B. Internal Standards

Hexadecane. Aldrich 99% pure hexadecane was used as recieved.

Ethyl benzoate. Ethyl benzoate was available in 100% pure condition from a previous study[115].

Propyl benzoate. ^{n}Propyl benzoate was available in 100% pure condition from a previous study[116].

Butyl benzoate. ^{n}Butyl benzoate was available in >99.5% pure condition from a previous study[116].

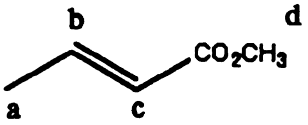
Heptyl benzoate. ^{n}Heptyl benzoate was available in >99.3% pure condition from a previous study[116].

Octyl benzoate. ^{n}Octyl benzoate was available in 100% pure condition from a previous study[117].

C. Quenchers

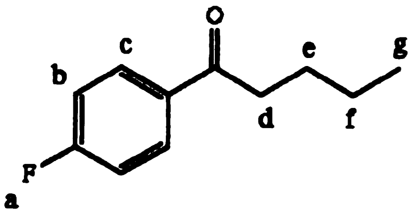
2,5-Dimethyl-hexa-2,4-diene. Aldrich 99% pure 2,5-dimethyl-2,4-hexadiene was allowed to sublime in the refrigerator.

Methyl trans-crotonate. A mixture of 80 g (0.93 mol) of crotonic acid and 30 ml absolute methanol (0.73 mol) was refluxed for 24 h with 2.2 ml concentrated H_2SO_4 [78,79] under Fisher conditions[78] to give, after two fractional distillations, 31% of the ester, bp= 116.5-116.9°C (lit. 119°/768 mm Hg)[79]. ^{1}H NMR ($CDCl_3$; 60 MHz): δ7.03 (dq, 1H, J_{ba}= 7.3; J_{bc}= 14 Hz, H_b), 5.88 (dq, 1H, J_{ca}= 2; J_{cb}= 8 Hz, H_c), 3.81 (s, 3H, H_d), 2.93 (dd, 3H, J_{ac}= 2; J_{ab}= 8 Hz, H_a). IR (CH_2Cl_2): 3054, 3016, 2950, 2910, 2836, 1722, 1662, 1434, 1308, 1206, 1176 cm^{-1}.

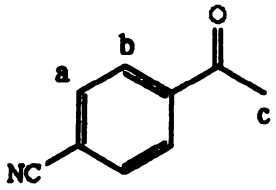


D. Ketones

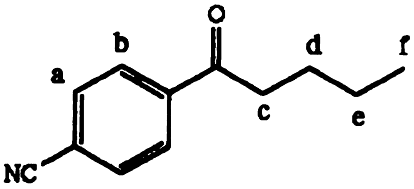
4'-Fluorovalerophenone. This compound was prepared by Friedel-Crafts acylation of fluorobenzene[80]. To a mechanically stirred mixture of 89 ml fluorobenzene (0.89 mol) and 104 g anhydrous $AlCl_3$ (0.78 mol) in 100 ml nitromethane at 0° was added 50 ml valeryl chloride (0.42 mol) over 5 min. The mixture was gradually warmed to room temperature with stirring over 1 h and then heated to a gentle reflux for 10 h. At the end of that time the hot mixture was cautiously poured into 100 ml 12% HCl and cracked ice. This mixture was extracted repeatedly into ether and the combined organic phase was washed with 1 N NaOH until the aqueous phase was colourless. After washing with water and brine and finally drying over $MgSO_4$, removal of the solvent left 65 g of a brown oil. Distillation of that material at 60-90°/0.1-1.0 mm Hg (lit. 95°/0.16 mm Hg)[81] gave a yellow liquid which was recrystallised from methanol in the refrigerator to give 37 g (49%) of a low-melting solid, pure by GC analysis. ^{1}H NMR (60 MHz; $CDCl_3$): δ7.95 (dd, 2H, J_{ca}= 5.0; J_{cb}= 8.0 Hz, H_c), 7.10 (t, 2H, $J_{ba} \approx J_{bc}$= 10.0 Hz, H_b), 2.93 (t, 2H, J_{de}= 7.0 Hz, H_d), 1.2-1.9 (complex, 4H, H_d; H_e), 0.93 (t, 3H, J_{fe}= 6.0 Hz, H_f). IR (CCl_4): 2966, 2942, 2881, 1792, 1606, 1460, 1413, 1225, 1212, 1186, 844 cm^{-1}. EI-MS: m/z= 181 ($M+1^+$), 180 ($M^{+\cdot}$), 151, 138, 123 (base), 95.



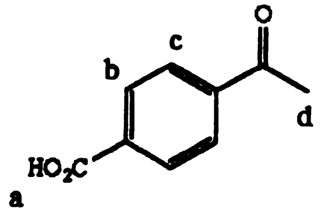
4'-Acetylbenzonitrile Prepared according to Siebert's procedure[81] in 40% yield by the treatment of 4'-fluoroacetophenone with 1.08 equivalents sodium cyanide in refluxing dimethylsulfoxide after crude distillation (bp= 90-120°C/ca. 0.8 mm Hg) and recrystallisation from hexane, mp= 52-54° (lit. 54-56°)[118]. ^{1}H NMR (60 MHz, $CDCl_3$); δ8.10 (d, 2H, J_{ba}= 8.0 Hz, H_b), 7.90 (d, 2H, J_{ab}= 8.0 Hz, H_a), 2.72 (s, 3H, H_c). IR (CCl_4): 2244, 1704, 1617, 1440, 1413, 1370, 1302, 1270, 855 cm^{-1}. EI-MS: m/z= 145 ($M^{+\cdot}$), 130 (base), 102, 75.



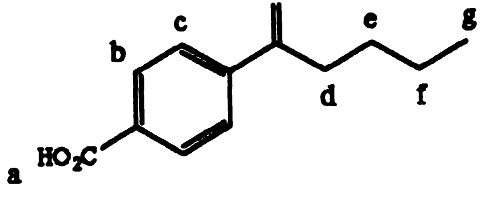
4'-Valerylbenzonitrile. Prepared according to Siebert's procedure[81] by the treatment of 4'-fluorovalerophenone with 1.15 equivalents of sodium cyanide in boiling dimethylsulfoxide in 59% yield after crude distillation (bp= 129-159°/0.8-0.9 mm Hg) and recrystallisation from hexane, mp= 34-35° (lit. 32-33°)[81]. ^{1}H NMR (60 MHz; $CDCl_3$): δ8.12 (d, 2H, J_{ba}= 5.0 Hz, H_b), 7.83 (d, 2H, J_{ab}= 5.0 Hz, H_a) 3.01 (t, 2H, J_{cd}= 8.0 Hz, H_c), 1.25-2.00 (complex, 4H, H_d; H_e), 0.98 (t, 3H, J_{fe}= 6.0 Hz, H_f). IR (CCl_4): 2965, 2937, 2879, 2236, 1694, 1471, 1412, 1214, 1022, 859 cm^{-1}. EI-MS: m/z= 187 ($M^{+\cdot}$), 154, 145, 130 (base), 102.



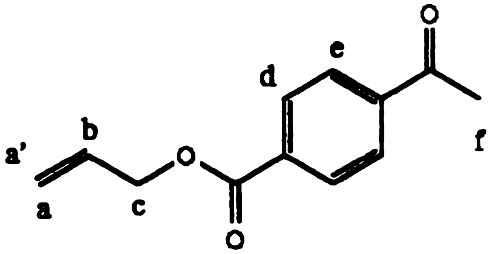
4'-Acetylbenzoic acid. According to a procedure adapted from the literature[82], 25 g of 4'-acetylbenzonitrile (0.172 mol) was heated to reflux for 15 h in 50 ml concentrated HCl, 150 ml glacial acetic acid and 30 ml water while monitoring by thin layer chromatography. At the end of that time, the solvent was removed by distillation, and the residual yellow oil was redissolved in 750 ml saturated $NaHCO_3$ and 2.25 l water. The aqueous solution was washed with ethyl ether, and the ether extracts discarded. The product was then precipitated from the bicarbonate solution by the careful addition of 2 N HCl, and recrystallised from copious amounts of water to give 14.9 g (53% yield) of fine white needles, mp= 206-208°C (lit. 205-206°)[82]. ^{1}H NMR (60 MHz; acetone-d_6): δ8.03 (s, 5H, H_a; H_b; H_c), 2.60 (s, 3H, H_d). IR (KBr pellet): 3067, 2567, 1712, 1677, 1437, 1300, 947, 861 cm^{-1}. EI-MS: m/z= 164 ($M^{+\cdot}$), 149 (base peak), 121.



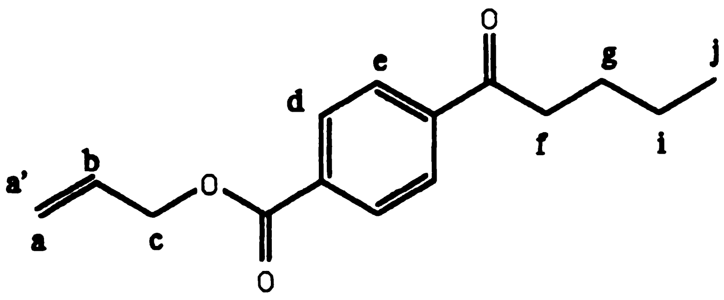
4'-Valerylbenzoic acid. The acylbenzoic acid was prepared by the procedure used by Siebert[81]. A solution of 18 g 4'-valerylbenzonitrile (0.096 mol) in 63 ml 30% aqueous potassium hydroxide and 18 ml ethanol was heated to reflux for 24 h. At the end of that time, the solution was rendered neutral by the addition of 6 N HCl. After cooling, the resulting precipitate was collected by suction filtration and washed with water to give 18.3 g (70%) of a tan solid, mp= 154.5-156.6° (lit. 155-157°)[81]. ^{1}H NMR (60 MHz; CDCl$_3$): δ8.08 (s, 4H, H$_b$; H$_c$), ca. 5.7 (broad s, 1H, H$_a$), 3.07 (t, 2H, J_{de}= 7.0 Hz, H$_d$), 1.1-2.1 (complex, 4H, H$_e$; H$_f$), 0.93 (t, 3H, J_{gf}= 6.0 Hz, H$_g$). IR (CHCl$_3$): 2547, 2677, 1647, 1467, 1367, 917, 861 cm^{-1}. EI-MS: m/z= 206 ($M^{+\cdot}$), 189, 177, 164, 161, 149 (base peak).



4'-Acetyl allyl benzoate. In a procedure modified from Mills[83], 0.89 ml $SOCl_2$ (0.012 mol) was added through a septum to a stirred, ice-cold solution of 2.00 g 4'-acetylbenzoic acid (0.012 mol) and 1.1 ml pyridine (0.014 mol) in 40 ml benzene under N_2. The resulting mixture was heated to reflux for 4 h, whereupon a red colour developed. The solution was decanted from a gummy precipitate, and the precipitate was in turn washed 3 times with benzene. The volume of the combined organic solution was reduced to ca. 10 ml by distillation at reduced pressure, cooled and added dropwise to a cooled, stirred solution of 0.95 ml allyl alcohol (0.0140 mol) and 1.1 ml pyridine in 25 ml petroleum ether under N_2. After stirring an additional 30 min at 0°, the solution was warmed to room temperature and stirred overnight. At the end of that time, the reaction mixture was suction filtered, and the filtrate was diluted with benzene and sequentially extracted 3 times each with aqueous 1% Na_2CO_3 and water. After drying with $MgSO_4$ and removing the solvent, this afforded a red oil, which was purified by column chromatography (Davisil 60; 30:70-EtOAc: hexanes) to give 1.30 g of a orangish oil (52% yield). ^1H NMR (300 MHz; $CDCl_3$): δ8.11 (d, 2H, J_{ed}= 8.7 Hz, H_e), 7.97 (d, 2H, J_{de}= 8.7 Hz, H_d), 6.02 (m, 1H, H_b), 5.39 (dt, 1H, J_{ac}= 1.6; J_{ab}= 17.2 Hz, H_a), 5.27 (dt, 1H, $J_{a'c}$= 1.5; $J_{a'b}$= 10.4 Hz, $H_{a'}$), 4.92 (broad t, 2H, J_{cb}= 5.7 Hz, H_c), 2.71 (s, 3H, H_f). ^{13}C NMR: δ199.1, 166.8, 141.7, 135.3, 133.2, 131.2, 129.5, 119.9, 67.1, 27.8. IR (CCl_4): 3097, 2957, 1730, 1697, 1659, 1115, 797 cm^{-1}. EI-MS: 204 ($M^{+\cdot}$), 183, 147 (base peak). UV-VIS (heptane): λ_{max}= 245, 285 nm.



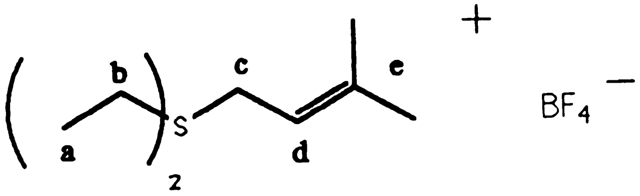
4'-Valeryl allyl benzoate. Prepared as was 4'-acetyl allyl benzoate^{83}, passage through Activity-1 basic alumina removed red colour completely. (57% yield) ^{1}H NMR (300 MHz; CDCl$_3$): δ8.11 (d, 2H, J_{ed}= 8.5 Hz, H_e), 7.97 (d, 2H, J_{de}= 8.5 Hz, H_d), 6.06 (m, 1H, H_b), 5.42 (dq, 1H, $J_{aa'}$≈ J_{ac}≈ 1.5; J_{ab}= 17.2 Hz, H_a), 5.28 (dq, 1H, $J_{a'a}$≈ $J_{a'c}$≈ 1.3; $J_{a'b}$= 10.4 Hz, $H_{a'}$), 4.81 (dt, 2H, J_{ca}≈ $J_{ca'}$≈ 1.4; J_{cb}= 5.7 Hz, H_c), 2.95 (t, 2H, J_{fg}= 7.4 Hz, H_f), 1.69 (quin, 2H, J_{gf}≈ J_{gi}= 7.7 Hz, H_g), 1.38 (sex, 2H, J_{ig}≈ J_{ij}= 7.4 Hz, H_i), 0.92 (t, 3H, J_{ji}= 7.3 Hz, H_j). ^{13}C NMR: δ200.1, 165.5, 140.4, 133.7, 132.0, 129.8, 127.9, 118.5, 65.7, 38.8, 25.8, 22.0, 13.5. IR (CCl$_4$): 2960, 2939, 2880, 1695, 1657, 1106, 800 cm^{-1}. EI-MS: m/z= 247, 246 ($M^{+\cdot}$), 217, 204, 189 (base peak).



Diethyl 3-methyl-2-butenyl sulfonium tetrafluoroborate.

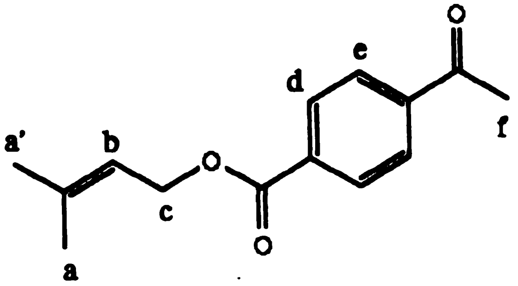
1. **Preparation of anhydrous hydrofluoroboric acid ethrate**[84a]. To 36.9 ml of dry ice-acetone-cooled boron trifluoride ethrate (0.300 mol) was added 6.0 ml cooled, liquified, anhydrous hydrogen fluoride (0.30 mol). The resulting pale orange liquid was stored under argon in a polyethylene vessel in a freezer and was generally used within 12 hours of its preparation.

2. **Preparation of the sulfonium salt.** In a modification of a procedure of Julia[84b], 48.5 g hydrofluoroboric acid ethrate (0.30 mol) was added in several portions to a stirred solution of 27.3 ml 3-methyl-2-butenyl alcohol (prenyl alcohol; 0.267 mol) and 58.4 ml diethyl sulfide (0.542 mol) in 45 ml CH_2Cl_2. The resulting solution was stirred at 0° for several hours and then at RT for ca. 18 h, whereupon two phases had formed. The lower phase was isolated, diluted with 100 ml CH_2Cl_2, dried with $MgSO_4$, leaving an orange oil after rotary evaporation of the solvent. The oil was triturated 4 times with extremely dry ether, and the remaining white solid was recrystallised from 1:1 absolute ethanol:ethyl ether to give, after drying overnight in a vacuum dessicator (P_2O_5), 53.3 g of crystals (81% yield), mp= 41.5-43.0 °C. ^1H NMR (60 MHz, $CDCl_3$) δ5.30 (broad t, 1H, J_{dc}= 8.0 Hz, H_d), 4.04 (d, 2H, J_{cd}= 8.0 Hz, H_c), 3.34 (q, 4H, J_{ba}= 9.0 Hz, H_b), 1.92 (s, 6H, H_e), 1.56 (t, 6H, J_{ab}= 11.0 Hz, H_a). IR (CH_2Cl_2): 1664, 3070, 691, 1065 cm^{-1}. EI-MS: m/z= 165 (3.3% relative intensity), 152 (7.5%), 130 (13.9%). Compare to dimethyl geranyl sulfonium tetrafluoroborate[84b], mp= 48-53°; ^1H NMR: δ5.40 (t, 2H, J= 8.0 Hz), 4.17 (d, 2H, J= 8.0 Hz), 2.92 (s, 6H), 1.85 (s, 3H).



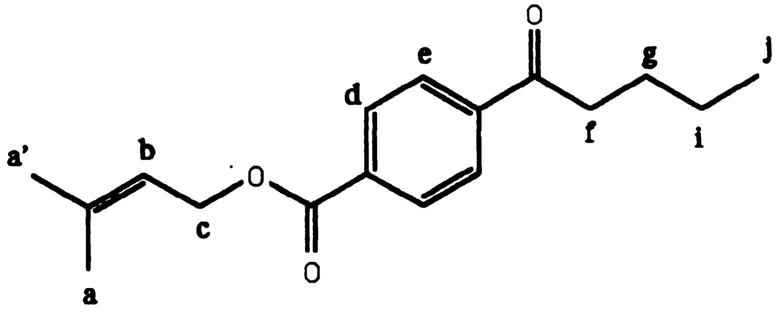
4'-Acetyl prenyl benzoate. A mixture of 3.50 g 4'-acetylbenzoic acid (0.0213 mol), 7.88 g diethyl prenyl sulfonium tetrafluoroborate (0.0320 mol) and 1.47 g oven-dried K_2CO_3 (0.0212 equivalents) in 250 ml anhydrous CH_2Cl_2 was stirred under a $CaCl_2$ guard tube for 4 days[85]. The reaction mixture was extracted 3 times with 70 ml 5% NaHCO, 4 times with water, dried with $MgSO_4$ and the passed rapidly through a short plug of Activity-1 basic alumina. After removal of the solvent, the product was purified by column chromatography (Davisil-60; 10:90-EtOAc:hexanes elutant) to give 1.12 g of a light yellow oil (23% yield), which could be recrystallised with some difficulty from hexane to give white crystals, mp= 36.6-37.7 °C. ^1H NMR (300MHz, $CDCl_3$): δ8.09 (d, 2H, J_{ed}= 7.5 Hz, H_e), 7.96 (d, 2H, J_{de}= 7.5 Hz, H_d), 5.44 (m, 1H, H_b), 4.81 (d, 2H, J_{cb} = 7.0 Hz, H_c), 2.60 (s, 3H, H_f), 1.76 (s, 3H, H_a), 1.74 (s, 3H, $H_{a'}$). ^{13}C NMR: δ198.0, 166.1, 140.3, 139.8, 134.5, 130.0, 128.3, 118.5, 62.2, 26.6, 25.6, 17.9. IR ($CHCl_3$): 3060, 2991, 1691, 1719, 1423, 841 cm^{-1}. EI-MS: m/z= 232 ($M^{+\cdot}$), 217, 199, 165, 147 (base peak). UV-VIS (heptane): $\lambda_{max} \approx$ 285 nm, $\epsilon_{285} \approx$ 17 000 $A \cdot \underline{M}^{-1} \cdot cm^{-1}$.

The 5% bicarbonate wash was treated with dilute acid to recover 1.96 g 4'-acetylbenzoic acid (56%) by filtration. The yield of product was possibly improved by addition of 2 equivalents of K_2CO_3, although it was not affected by an increase in reaction time past 3 days, nor by an increase of the equivalents of sulfonium salt past 1.0.



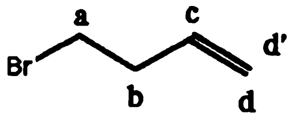
4'-Valeryl prenyl benzoate. In a manner similar to that used in the preparation of 4'-acetyl prenyl benzoate[85], this compound was prepared as fine white needles of mp= 37.2-38.3°C in 29% yield. ^{1}H NMR (300MHz, $CDCl_3$): δ8.08 (d, 2H, J_{ed}= 8.7 Hz, H_e), 7.95 (d, 2H, J_{de}= 8.7 Hz, H_d), 5.43 (m, 1H, H_b), 4.80 (d, 2H, J_{cb}= 7.3 Hz, H_c), 2.95 (t, 2H, J_{fg}= 7.4 Hz, H_f), 1.76 (s, 3H, H_a), 1.74 (s, 3H, $H_{a'}$), 1.68 (quin, 2H, $J_{gf} \approx J_{gi}$= 7.3 Hz, H_g), 1.37 (sex, 2H, $J_{ig} \approx J_{ij}$= 7.2 Hz, H_i), 0.91 (t, 3H, J_{ji}= 7.3 Hz, H_j). ^{13}C NMR: δ200.4, 166.1, 140.4, 139.8, 134.2, 130.0, 128.0, 118.5, 62.2, 38.5, 26.0, 25.6, 22.2, 17.9, 13.6. IR ($CHCl_3$): 2965, 1727, 1696, 1273, 1104, 830 cm^{-1}. EI-MS (25 eV): m/z= 232, 217, 207, 189, 164, 162, 149.

An additional 1.03 g starting material (31%) was recovered by acidification of the 5% bicarbonate wash and filtration.



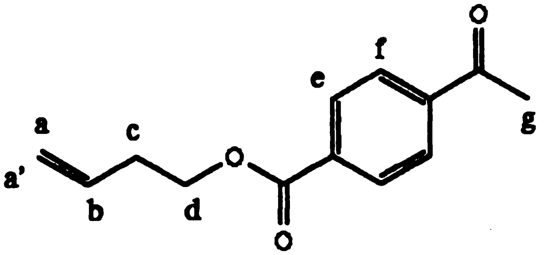
4-Bromo-1-butene. CAUTION: Due to the high toxicity of the hexamethylphosphoric triamide[119] (HMPA) used in this procedure, the entire reaction and work-up were conducted in a well-ventilated hood, the interior surfaces of which were lined with 2-3 layers of paper towels. Rubber gloves, safety goggles and a disposible lab coat were worn. Dirty glassware was rinsed with water or acetone, and the washings were isolated in a bottle. Solid waste was contained in double-lined plastic bags. All waste materials were removed and disposed of by qualified personel.

The bromoalkene was prepared according to the general procedure of Kraus and Landgrebe[87] for ω-bromo-1-alkenes. A 3-necked flask outfitted with a dropping funnel, stillhead/condenser and magnetic stirrer was charged with 140 ml 1,4-dibromobutane (1.17 mol) and afterwards heated to 195-205° on an oil bath. To this was added 185 ml HMPA (1.06 mol) at a rate of ca. 1-2 drops/sec. Distillation of the crude product into a dry ice-acetone cooled recieving flask (bp= 80-110°) began ca. 10 min. after starting the addition of HMPA. It was redistilled, bp= 94-96° (lit. 98-100°)[87] to give 89.0 g (56% yield) of a clear liquid. ^{1}H NMR (60 MHz, $CDCl_3$): δ5.73 (m, 1H, H_c), 5.13 (d, 1H, J_{dc}= 14.0 Hz, H_d), 5.00 (broad s, 1H, $H_{d'}$), 3.47 (t, 2H, J_{ab}= 10.0 Hz, H_a), 2.65 (q, 2H, $J_{ba} \approx J_{bc} \approx$ 8.0 Hz, H_b).



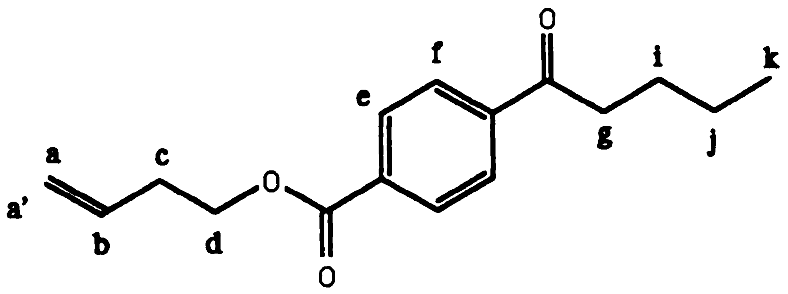
4'-Acetyl 3-butenyl benzoate. CAUTION: This procedure also called for the use of HMPA. See preparation 4-bromo-1-butene for precautions.

Following a proceedure developed by Pfeffer[86], to a mixture of 0.82 g 4'-acetylbenzoic acid (0.0050 mol) and 0.30 g pulverised, anhydrous KOH (0.0053 mol) in 20 ml anhydrous 1:1- HMPA:ethanol was added 1.02 ml 4-bromo-1-butene (0.010 mol). After heating to reflux under a $CaCl_2$ guard tube for 2 days, the reaction mixture was treated with an another 1.02 ml 4-bromo-1-butene and refluxed for a further 2 days. The progress of the reaction was monitored by t.l.c.; it could also be followed visually by the disappearance of undissolved 4'-acetyl potassium benzoate. Other experiments not presented in this Thesis showed that this type of reaction could also be implemented using the same number of equivalents of dimethyltetrahydropyrimidione instead of HMPA. The reaction mixture was then poured into 50 ml water and normalised by the addition of 1 N HCl. The aqueous solution was extracted 4 times with ethyl ether, and the combined organic solution was washed 4 times with 10 ml saturated aqueous $NaHCO_3$, 3 times with water, and 3 times with brine. After drying with $MgSO_4$ and removal of the solvent under reduced pressure, the resulting yellow oil was partially purified by column chromatography (40:60 - EtOAc:hexanes) and finally by Kuegelrohr distillation (bp≈ 110°C /0.02 mm Hg) to give 0.64 g of a clear oil (59% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ8.06 (d, 2H, J_{fe}= 8.0 Hz, H_f), 7.95 (d, 2H, J_{ef}= 8.0 Hz, H_e), 5.86 (m, 1H, H_b), 5.14 (dt, 1H, J_{ac}= 1.6; J_{ab}= 16.4 Hz, H_a), 5.07 (dt, 1H, $J_{a'c}$≈ 1.5; $J_{a'b}$= 10.3 Hz, $H_{a'}$), 4.35 (t, 2H, J_{dc}= 6.0 Hz, H_d), 2.58 (s, 3H, H_g), 2.49 (q, 2H, J_{cb}≈ J_{cd}= 7.4 Hz, H_c). ^{13}C NMR: δ197.6, 165.7, 140.2, 134.1, 133.9, 129.7, 128.1, 117.4, 64.1, 32.7, 26.4. IR (CCl_4): 3082, 2962, 1742, 1698, 1262, 1277, 832 cm^{-1}. EI-MS: m/z= 218 ($M^{+\cdot}$), 203, 177, 164, 149, 147 (base peak).

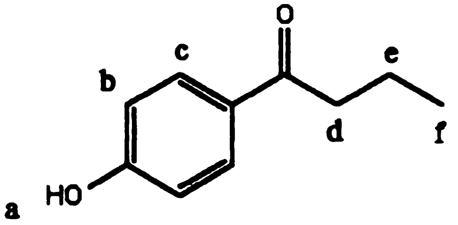


4'-Valeryl 3-butenyl benzoate. CAUTION: This procedure also caled for the use of HMPA. See preparation of 4-bromo-1-butene for precautions.

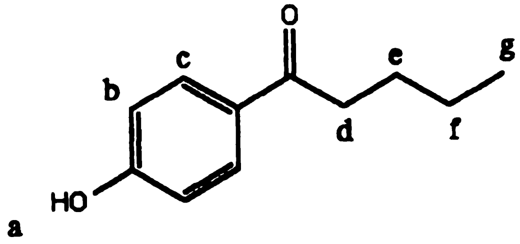
A mixture of 3.00 g 4'-valeryl benzoic acid (0.0150 mol) and 0.89 g pulverised KOH (0.0159 mol) in 60 ml 1:1 - HMPA:ethanol was treated with 4-bromo-1-butene in a mannor analogous to that used for the preparation of 4'-acetyl 3-butenyl benzoate[86]. Purification by column chromatography (Davisil 60; 50:50 EtOAc:hexanes) gave 2.53 g of a pale yellow oil (65% yield). ^{1}H NMR (300 MHz $CDCl_3$): δ8.06 (d, 2H, J_{fe}= 8.8 Hz, H_f), 7.95 (d, 2H, J_{ef}= 8.8 Hz, H_e), 5.82 (m, 1H, H_b), 5.13 (dt, 1H, J_{ac}= 1.7; J_{ab}= 17.2 Hz, H_a), 5.07 (dt, 1H, $J_{a'c}$≈ 1.4; $J_{a'b}$= 10.6 Hz, H$_{a'}$), 4.36 (t, 2H, $J_{dc} \approx$ 6.4 Hz, H$_d$), 2.94 (t, 2H, J_{gi}= 7.4 Hz, H$_g$), 2.49 (tq, 2H, $J_{ca} \approx J_{ca'} \approx$ 1.6; $J_{cd} \approx J_{cb} \approx$ 6.6 Hz, H$_c$), 1.67 (quin, 2H, $J_{ig} \approx J_{ij}$= 7.5 Hz, H$_i$), 1.36 (sex, 2H, $J_{ji} \approx J_{jk}$= 7.5 Hz, H$_j$), 0.90 (t, 3H, J_{kj}= 7.3 Hz, H$_k$). ^{13}C NMR: δ200.3, 140.4, 134.0, 129.9, 128.0, 117.6, 64.2, 38.4, 32.9, 26.0, 22.1, 13.6. IR (CCl_4): 3097, 2907, 1733, 1701, 1280, 1112, 862 cm^{-1}. EI-MS: m/z= 218, 214, 203 (base), 189, 164, 161, 149.



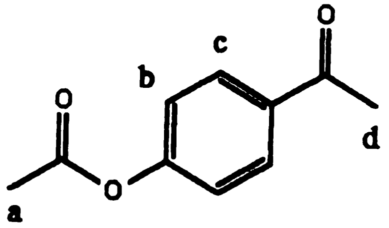
4'-Butyrylphenol. A mechanically stirred mixture of 38 g phenol (0.40 mol), 39 g butyric acid (0.40 mol), and 200 g polyphosphoric acid was heated 10 min in a boiling water bath[88]. The reaction mixture was then cooled in an ice-water bath, and rendered basic to red litmus paper by the careful addition of chilled 10 N NaOH and NaOH pellets. After diluting to ca. 3 l to dissolve phenoxide salts, the aqueous solution was washed twice with ether and recooled in an ice-water bath. It was then treated with concentrated HCl until the persistence of a deep yellow colour in solution was noted. This solution was extracted repeatedly with ethyl ether (followed by t.l.c.), and the combined organic solution was washed twice each with 10% aqueous $NaHCO_3$, water, and brine. After drying with $MgSO_4$ and rotary evaporation of the solvent, the crude product was recrystallised from 3:1 - petroleum ether:benzene to afford 27.6 g (42% yield) of white crystals, mp= 90.0-91.0°C (lit. 91°)[89]. ^{1}H NMR (250 MHz; $CDCl_3$): δ8.13 (s, 1H, H_a), 7.97 (d, 2H, J_{cb}= 9.0 Hz, H_c), 7.02 (d, 2H, J_{bc}= 9.0 Hz, H_b), 2.94 (t, 2H, J_{de}= 7.0 Hz, H_d), 1.78 (sex, 2H, $J_{ed} \approx J_{ef}$= 7.5 Hz, H_e), 1.01 (t, 3H, J_{fe}= 8.0 Hz, H_f). IR (CH_2Cl_2): 3571, 3333, 3071, 2969, 2938, 2878, 1678, 1607, 1590, 1516, 1414, 1267, 1171, 819 cm^{-1}. EI-MS: m/z= 164 ($M^{+\cdot}$), 149, 136, 121 (base).



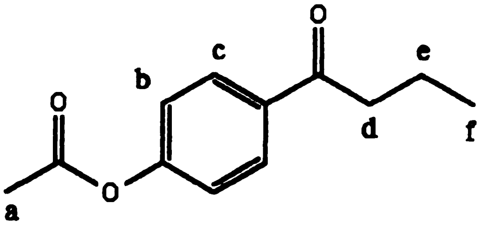
4'-Valerylphenol. In a manner similar to that used in the preparation of 4'-hydroxybutyrophenone[88], valeric acid, phenol, and polyphosphoric acid were reacted to give, after work-up and recrystallisation, 31% yield of white crystals, mp= 59.8-61.0°C (lit. 62°)[77]. ^{1}H NMR (60 MHz, $CDCl_3$): δ8.39 (s, 1H, H_a), 8.04 (d, 2H, J_{cb}= 8.0 Hz, H_c), 7.10 (d, 2H, J_{bc}= 10.0 Hz, H_b), 3.05 (t, 2H, J_{de}= 7.0 Hz, H_d), 1.2- 2.0 (complex, 4H, H_e; H_f), 1.06 (t, 3H, J_{gf}= 6.0 Hz, H_g). IR (CH_2Cl_2): 3572, 3332, 3062, 2962, 2934, 2868, 1672, 1612, 1588, 1270, 1166, 842 cm^{-1}. EI-MS: m/z= 220 ($M^{+\cdot}$), 175, 163, 149, 136, 121 (base).



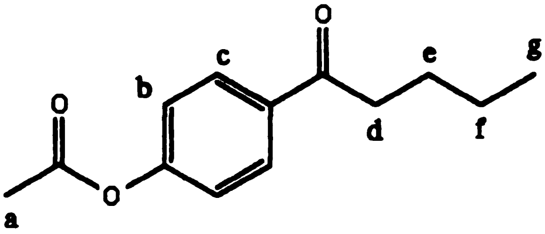
4'-Acetylphenyl acetate. Esterification of 8.2 g 4'-acetylphenol (0.060 mol) was accomplished under Schotten-Baumen conditions[78]. The phenol was treated first with cold 14 N NaOH (1.5 equivalents) and then with 1.08 g acetic anhydride (1.0 equivalent). Following work-up and recrystallisation from ethanol, this gave 5.30 g (50% yield) of white plates, mp= 50.0-51.5°C (lit. 54°)[79]. ^1H NMR (300 MHz, $CDCl_3$): δ7.97 (d, 2H, J_{cb}= 8.5 Hz, H_c), 7.17 (d, 2H, J_{bc}= 8.5 Hz, H_b), 2.67 (s, 3H, H_d), 2.40 (s, 3H, H_a). ^{13}C NMR: 196.7, 168.5, 154.1, 134.3, 129.5, 121.4, 25.7, 20.2. IR (CCl_4): 1773, 1697, 1205, 1167, 851 cm^{-1}. EI-MS: m/z= 178, 136, 121 (base). UV-VIS (CH_3OH): λ_{max}= 247.5 nm; $\epsilon_{247.5}$= 15 000 $A \cdot \underline{M}^{-1} \cdot cm^{-1}$.



4'-Butyrylphenyl acetate. Esterification of 8.02 g 4'-butyrylphenol (0.050 mol) was accomplished by treatment with 14 N NaOH followed by acetic anhydride[90]. Following basic work-up and recrystallisation from 9:1 - petroleum ether:benzene, this gave 7.45 g (72% yield) of white crystals, mp= 28-29°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ8.20 (d, 2H, J_{cb}= 8.6 Hz, H_c), 7.20 (d, 2H, J_{bc}= 8.6 Hz, H_b), 2.88 (t, 2H, J_{de}= 7.6 Hz, H_d), 2.26 (s, 3H, H_a), 1.72 (sex, 2H, $J_{ed} \approx J_{ef}$= 7.5 Hz, H_e), 0.95 (t, 3H, J_{fe}= 6.9 Hz, H_f). ^{13}C NMR: δ199.3, 169.0, 154.3, 134.7, 129.7, 121.7, 40.1, 20.7, 17.3, 13.4. IR (CCl_4): 2969, 2882, 1773, 1694, 1603, 1372, 1200, 1165, 841 cm^{-1}. EI-MS: m/z= 164 ($M^{+\cdot}$), 149, 136, 122, 121 (base), 93. UV-VIS (CH_3OH): λ_{max}= 205; 247 nm, ϵ_{205}= 14 000; ϵ_{247}= 14 000; ϵ_{313}= 85 $A \cdot \underline{M}^{-1} \cdot cm^{-1}$.

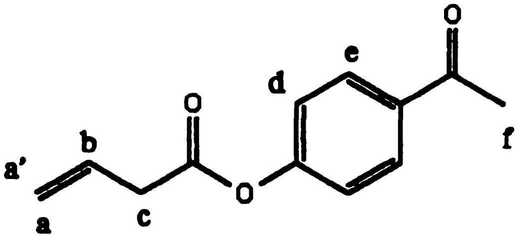


4'-Valerylphenyl acetate. Esterification of 8.90 g 4'-valerylphenol (0.050 mol) with 14 N NaOH and acetic anhydride[90] followed by slow recrystallisation from petroleum ether-benzene gave 7.22 g of large, white rhombohedral crystals, mp= 26.2-27.1°C (66% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ8.02 (d, 2H, J_{cb}= 8.8 Hz, H_c), 7.20 (d, 2H, J_{bc}= 8.8 Hz, H_b), 2.83 (t, 2H, J_{de}= 7.4 Hz, H_d), 2.19 (s, 3H, H_a), 1.61 (quin, 2H, $J_{ed} \approx J_{ef}$= 7.5 Hz, H_e), 1.30 (sex, 2H, $J_{fe} \approx J_{fg}$= 7.5 Hz, H_f) 0.84 (t, 3H, J_{gf}= 7.4 Hz, H_g). ^{13}C NMR: δ199.2, 168.8, 154.2, 134.5, 129.5, 121.6, 37.8, 25.9, 21.9, 20.5, 13.4. IR (CCl_4): 2963, 2842, 1777, 1694, 1603, 1372, 1198, 1167, 847 cm^{-1}. EI-MS (25 eV): m/z= 218 ($M^{+\cdot}$), 203 (base), 189, 164, 162, 149, 147 (lit. spectra)[92]. UV-VIS (heptane): λ_{max}= 204; 246 nm, ϵ_{204}= 14 000; ϵ_{246}= 12 000; ϵ_{313}= 56 A·$\underline{M}^{-1}$·cm^{-1}. Phosphorescence emission (313 nm excitation, chopper rate= ca. 1 700 c.p.s., 77°K): 2-methyltetrahydrofuran ([ketone]= 0.000092 $\underline{M}$): $\lambda_{o,o}$= 394 nm, 5:1 - methanol:ethanol ([ketone]= 0.00012 $\underline{M}$): $\lambda_{o,o}$= 397 nm.



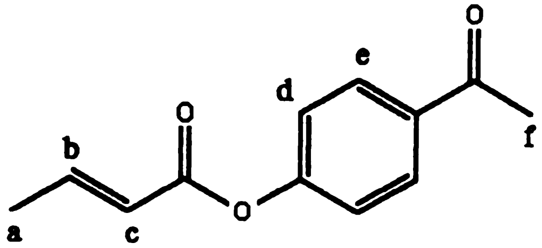
4'-Acetylphenyl 3-butenoate. The 4'-acetylphenol was esterified with 4'-dimethylaminopyridine (DMAP) and dicyclohexylcarbodiimide (DCC) according to the procedure of Alexanian[93]. To a solution of 0.75 g 4'-acetylphenol (0.0055 mol), 0.43 g vinyl acetic acid (0.0050 mol) and 0.030 g DMAP (0.00025 mol) in 15 ml dry CH_2Cl_2 under a $CaCl_2$ guard tube was added 1.13 g DCC (0.0055 mol). After stirring at room temperature for ca. 1/2 h, an equal volume of hexane was added and stirring was continued for another 1/2 h. At the end of that time, the reaction mixture was filtered from a white precipitate, and the filtrate was quickly washed three times successively with 5 ml each of 5% aqueous acetic acid, water, 5% aqueous $NaHCO_3$, water, and then finally once with brine. After drying with Na_2CO_3 and then rapidly filtering the solution through a ca. 2 cm plug of Activity-1 neutral alumina, the solvent was removed at reduced pressure and room temperature, affording

0.61 g of a clear oil (60% yield), contaminated with traces of 4'-acetylphenyl trans-crotonate (vide infra). ^{1}H NMR (300 MHz, $CDCl_3$): δ7.98 (d, 2H, J_{ed}= 8.9 Hz, H_e), 7.20 (d, 2H, J_{de}= 8.9 Hz, H_d), 5.95 (ddt, 1H, J_{bc}= 6.9; $J_{ba'}$= 10.1; J_{ba}= 17.1 Hz, H_b), 5.22 (dq, 1H, $J_{aa'} \approx J_{ac} \approx$ 1.5; J_{ab}= 17.1 Hz, H_a), 5.20 (dq, 1H, $J_{a'a} \approx J_{a'c} \approx$ 1.3; $J_{a'b}$= 10.1 Hz, $H_{a'}$), 3.29 (dt, 2H, $J_{ca} \approx J_{ca'} \approx$ 1.4; J_{cb}= 6.8 Hz, H_c), 2.58 (s, 3H, H_f). ^{13}C NMR: δ197.1, 169.5, 154.4, 134.7, 129.9, 129.2, 121.6, 119.4, 38.6, 26.1. IR (CH_2Cl_2): 3065, 2938, 1763, 1688, 1601, 1428, 842 cm^{-1}. UV-VIS (CH_3OH): λ_{max}= 247.8 nm; $\epsilon_{247.8}$= 13 000 $A\cdot\underline{M}^{-\forall}J\{ \; ^{=\forall}=$



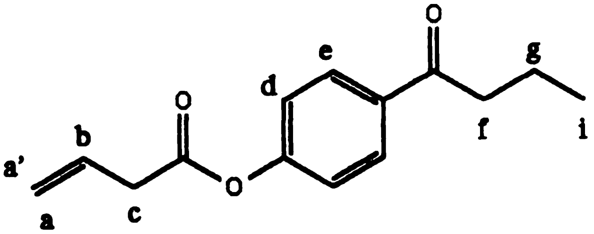
The amount of the trans-crotonate isomer present in the product ester was determined by comparison of the integration of its signal in the ^{1}H NMR spectrum at δ1.96 [93] (vide infra) to that of the β,γ-unsaturated isomer at δ3.29. In the initally isolated ester, this was usually below 5.0%. Although relatively stable in the neat in silanized glassware at 0°C, it decomposed rapidly to the crotonate isomer in solution. Therefore, it was used immediately upon isolation. All attempts to completely remove this impurity- silica and alumina chromatography, distillation from silanized glassware washed with dilute ammonium hydroxide, (bp= 80-110°C/0.002 mm Hg), Diels-Alder reaction with cyclopentadiene- only resulted in further isomerisation. Also see "Photolysis Procedures" for additional considerations.

4'-Acetylphenyl trans-crotonate. In a procedure similar to the one used for the preparation of 4'-acetylphenyl 3-butenoate[93], trans-crotonic acid and 4'-acetylphenol were coupled to give, after recrystallisation from benzene/hexane, 79% of white crystals, mp= 67.8-68.4°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.98 (d, 2H, J_{ed}= 8.0 Hz, H_e) 7.20 (d, 2H, J_{de}= 8.0 Hz, H_d), 7.19 (m, 1H, H_b), 6.03 (broad d, 1H, J_{cb}= 14.7 Hz, H_c), 2.58 (s, 3H, H_f), 1.96 (dd, 3H, J_{ac}= 1.7; J_{ab}= 6.9 Hz, H_a). ^{13}C NMR: δ197.3, 164.4, 154.8, 148.1, 134.7, 130.0, 121.9, 121.8, 32.5, 30.6, 26.3, 26.1, 24.4, 18.0. IR (CH_2Cl_2): 3022, 2917, 2822, 1740, 1688, 1167, 1156, 862 cm^{-1}. EI-MS: m/z= 204 ($M^{+\cdot}$), 121, 111, 92, 77, 69 (base). UV-VIS (CH_3OH): λ_{max}= 248.5 nm; $\epsilon_{248.5}$= 16 000 $A \cdot \underline{M}^{-1} \cdot cm^{-1}$.



4'-Butyrylphenyl 3-butenoate. In a procedure similar to that used for the preparation of 4'-acetylphenyl 3-butenoate[93], a colourless oil was isolated after work-up in 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ7.95 (d, 2H, J_{ed}= 7.5 Hz, H_e), 7.15 (d, 2H, J_{de}= 7.5 Hz, H_d), 5.98 (ddt, 1H, J_{bc}= 6.9; $J_{ba'}$= 10.2; J_{ba}= 17.2 Hz, H_b), 5.25 (dq, 1H, $J_{aa'} \approx J_{ac} \approx$ 1.3;

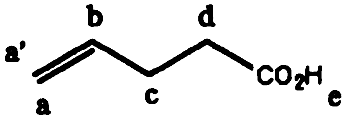
J_{ab}= 17.2 Hz, H_a), 5.23 (dq, 1H, $J_{a'a} \approx J_{a'c} \approx$ 1.4; $J_{a'b}$= 10.2 Hz, $H_{a'}$), 3.22 (dt, 2H, $J_{ca} \approx J_{ca'} \approx$ 1.4; J_{cb}= 6.9 Hz, H_c), 2.88 (t, 2H, J_{fg}= 7.3 Hz, H_f), 1.72 (sex, 2H, $J_{gf} \approx J_{gi}$= 7.3 Hz, H_g), 0.95 (t, 3H, J_{ig}= 7.4 Hz, H_i). ^{13}C NMR: δ199.1, 169.5, 154.2, 134.7, 129.6, 129.3, 121.6, 119.4, 40.0, 38.6, 17.2, 13.4. IR (CH_2Cl_2): 3112, 2969, 1763, 1688, 1603, 1512, 1414, 842 cm^{-1}. EI-MS (25 eV): m/z= 232 ($M^{+\cdot}$), 204, 189, 164, 147, 136, 121, 68 (base). UV-VIS (CH_3OH): λ_{max}= 205; 246.5 nm, ϵ_{205}= 13 000; $\epsilon_{246.5}$= 14 000; ϵ_{313}= 120 A·$\underline{M}^{-1}$·cm^{-1}.



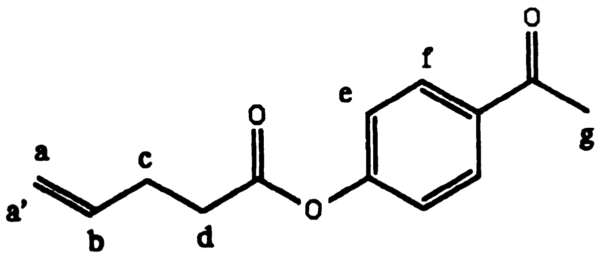
The amount of 4'-butyrylphenyl trans-crotonate initally present, as assayed by ^{1}H NMR spectroscopy immediately after preparation, was compareable to the 4'-acetylphenyl ester case.

4-Pentenoic acid. Grignard reaction of 3-butenyl magnesium bromide with CO_2 gas according to a procedure in the literature[94] afforded the acid in 35% yield after distillation, bp= 89-91°C/ ~17 mm Hg (lit. 95-97°/ 15 mm Hg)[94]. The reaction was initiated by addition of a catalytic amount of I_2. Carbon dioxide gas was generated from dry ice, passed through concentrated H_2SO_4 and afterwards anhydrous $CaCl_2$, and finally bubbled through the stirred solution overnight. ^{1}H NMR

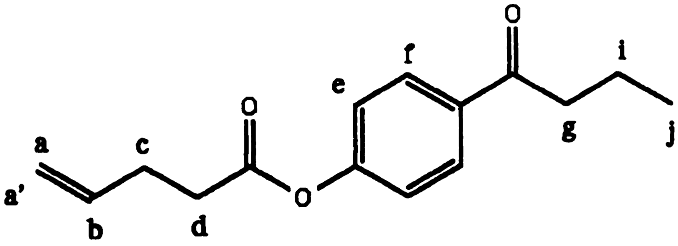
(300MHz, $CDCl_3$): δ10.1 (broad s, 1H, H_e), 5.84 (ddt, 1H, J_{bc}= 6.2; $J_{ba'}$= 10.3; J_{ba}= 17.1 Hz, H_b), 5.09 (dq, 1H, J_{ac}≈ $J_{aa'}$≈ 1.6; J_{ab}= 17.1 Hz, H_a), 5.03 (dq, 1H, $J_{a'c}$≈ $J_{a'a}$≈ 1.4; $J_{a'b}$= 10.3 Hz, $H_{a'}$), 2.44 (d, 2H, J_{dc}≈ 5.9 Hz, H_d), 2.39 (q, 2H, J_{cb}≈ J_{cd}≈ 6.3 Hz, H_c). IR (CH_2Cl_2): 3508, 3090, 3070, 2990, 2934, 2674, 1712, 1642, 1434, 1418, 1288, 1262, 1222 cm^{-1}. EI-MS: m/z= 100 ($M^{+\cdot}$), 83, 55 (base).



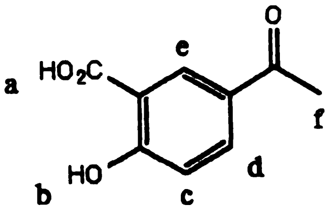
4'-Acetylphenyl 4-pentenoate. In a procedure like that used for the preparation of 4'-acetylphenyl 3-butenoate[93], a colourless oil was isolated in 59% yield after work-up and column chromatography (Davisil 60; 10:90 to 40:60 - ethyl acetate:hexanes). ^1H NMR (300MHz, $CDCl_3$): δ7.93 (d, 2H, J_{fe}= 7.0 Hz, H_f), 7.13 (d, 2H, J_{ef}= 7.0 Hz, H_e), 5.85 (ddt, 1H, J_{bc}= 6.5; $J_{ba'}$= 10.3; J_{ba}= 17.1 Hz, H_b), 5.10 (dq, 1H, $J_{aa'}$≈ J_{ac}≈ 1.6; J_{ab}= 17.1 Hz, H_a), 5.03 (dq, 1H, $J_{a'a}$≈ $J_{a'c}$≈ 1.4; $J_{a'b}$= 10.3 Hz, $H_{a'}$), 2.64 (t, 2H, J_{dc}= 7.0 Hz, H_d), 2.53 (s, 3H, H_g), 2.45 (broad q, 2H, J_{cb}≈ J_{cd}= 6.4 Hz, H_c). ^{13}C NMR: δ197.1, 171.2, 154.6, 136.2, 134.8, 130.0, 121.8, 116.1, 33.3, 28.4, 26.3. IR (CH_2Cl_2): 3067, 3011, 2932, 1761, 1688, 1646, 1237, 1208, 863 cm^{-1}. EI-MS: m/z= 218 ($M^{+\cdot}$), 203, 161, 147, 137, 121, 83, 55 (base). UV-VIS (CH_3OH): λ_{max}= 248.0 nm; ϵ_{248}= 14 000 $A\cdot\underline{M}^{-1}\cdot cm^{-1}$.



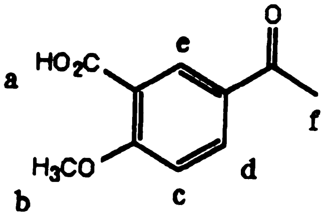
4'-Butyrylphenyl 4-pentenoate. Following a proceedure like that used to prepare 4'-acetylphenyl 3-butenoate[93], a colourless oil was isolated in 84% yield after work-up and column chromatography (Davisil 60; 10:90 to 40:60 - ethyl acetate: hexanes). ^{1}H NMR (300MHz, $CDCl_3$): δ7.94 (d, 2H, J_{fe}= 8.6 Hz, H_f), 7.13 (d, 2H, J_{ef}= 8.6 Hz, H_e), 5.85 (ddt, 1H, J_{bc}= 6.6; $J_{ba'}$= 10.2; J_{ba}= 17.0 Hz, H_b), 5.10 (dq, 1H, $J_{aa'} \approx J_{ac} \approx$ 1.5 Hz, H_a), 5.04 (dq, 1H, $J_{a'a} \approx J_{a'c} \approx$ 1.3; $J_{a'b}$= 10.2 Hz, $H_{a'}$), 2.87 (t, 2H, J_{gi}= 7.3 Hz, H_g), 2.64 (t, 2H, J_{dc}= 7.2 Hz, H_d), 2.46 (broad q, 2H, $J_{cd} \approx J_{cb}$= 7.0 Hz, H_c), 1.71 (sex, 2H, $J_{ig} \approx J_{ij}$= 7.4 Hz, H_i), 0.95 (t, 3H, J_{ji}= 7.4 Hz, H_j). ^{13}C NMR: δ199.3, 171.2, 154.4, 136.2, 134.7, 129.7, 121.8, 116.1, 40.2, 33.3, 28.5, 17.4, 13.5. IR (CH_2Cl_2): 3085, 2969, 2938, 2878, 1761, 1688, 1644, 1208, 1167, 1136, 842 cm^{-1}. EI-MS: m/z= 247 ($M+1^+$), 246 ($M^{+\cdot}$), 218, 203, 165, 147, 136, 121, 83, 55 (base). UV-VIS (CH_3OH): λ_{max}= 205; 247.5 nm, ϵ_{205}= 16 000; $\epsilon_{247.5}$= 17 000; ϵ_{313}= 88 A·$\underline{M}^{-1}$·cm^{-1}



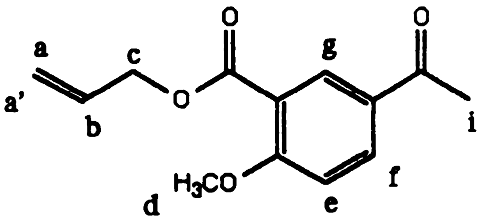
5'-Acetyl-2'-hydroxybenzoic acid. A modification of a known procedure for the Fries rearrangement of acetyl salicylic acid[96] was employed to obtain this compound. A suspension of 35 g anhydrous aluminum chloride (0.26 mol) as additional dessicant in dry nitrobenzene (distilled from P_2O_5) was stirred for 1 h at RT under N_2. To this slurry was added an additional 17 g aluminum chloride (0.13 mol) and 15 g acetyl salicylic acid (0.083 mol). After stirring at RT for another hour, the reaction mixture was carefully poured onto cracked ice and 25 ml concentrated HCl. The nitrobenzene was removed by steam distillation, and the crude product was collected by suction filtration. Recrystallisation twice from 40:60 ethanol:water then gave 7.7 g of white needles (51% yield), mp= 216.5-217.0° (lit. 216-217°)[96]. ^{1}H NMR (60 MHz, DMSO-d_6): δ12.30 (broad s, 2H, H_a; H_b), 8.41 (d, 1H, J_{ed}= 2.0 Hz, H_e), 8.09 (dd, 1H, J_{de}= 2.0; J_{dc}= 8.0 Hz, H_d), 7.07 (d, 1H, J_{cd}= 8.0 Hz, H_c), 2.62 (s, 3H, H_f). IR (KBr pellet): 3862, 3842, 2902, 2602, 2342, 2322, 1682, 1532, 842, 817 cm^{-1}. EI-MS: m/z= 180 ($M^{+\cdot}$), 165, 162, 147 base).



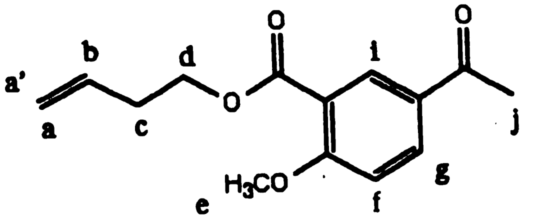
5'-Acetyl-2'-methoxybenzoic acid. The title compound was prepared according to the procedure of Kranichfeldt[97]. To a solution of 2.0 g 5'-acetyl-2'-hydroxybenzoic acid (0.0111 mol) in 11.1 g 10% aqueous NaOH (0.0278 mol) was added 3.15 ml dimethylsulfate (0.0333 mol). This mixture was heated under reflux for 1/2 h and then cooled to RT. Treatment with NaOH solution and dimethylsulfate, followed by heating, was repeated two more times. A further 11.1 g of 10% NaOH was then added, and the reaction mixture was heated under reflux an additional 1/2 h. Finally, 0.93 g CaO (0.0166 mol) was added, followed by refluxing for ca. 2.5 h. The cooled mixture was filtered from calcium salts, the filtrate was re-acidified with 2 N HCl and extracted repeatedly into ether. The combined ethereal extracts were washed with water, then saturated NaCl solution and dried over $MgSO_4$ to give, after evaporation of the solvent under reduced pressure and recrystallisation from 50:50 - ethanol:water, 1.49 g (70% yield) of white needles, mp= 148.5-150°C (lit. 152°)[85]. ^1H NMR ($CHCl_3$, 60 MHz): δ9.20 (broad s, 1H, H_a), 8.62 (d, 1H, J_{ed}= 2.0 Hz, H_e), 8.12 (dd, 1H, J_{de}= 2.0; J_{dc}= 9.0 Hz, H_d), 7.14 (d, 1H, J_{cd}= 9.0 Hz, H_c), 4.19 (s, 3H, H_b), 2.65 (s, 3H, H_f). IR (CH_2Cl_2): 3330, 3080, 2956, 2858, 1761, 1690, 1616, 1432, 1394, 837 cm^{-1}. EI-MS: m/z= 194 ($M^{+\cdot}$), 179 (base peak), 165, 161, 151, 147.



5'-Acetyl-2'-methoxy allyl benzoate. In a procedure like that used for the preparation of 4'-butyrylphenyl 3-butenoate[93], the title compound was obtained in 10% yield after passage through ca. 1.5 cm basic alumina, mp= 43.7-44.7 °C. ^{1}H NMR (300MHz, $CDCl_3$): δ8.39 (d, 1H, J_{gf}= 2.0 Hz, H_g), 8.10 (dd, 1H, J_{fg}= 2.0; J_{fe}= 8.8 Hz, H_f), 7.08 (d, 1H, J_{ef}= 8.8 Hz, H_e), 5.98 (m, 1H, H_b), 5.37 (dt, 1H, J_{ac}= 1.6; J_{ab}= 17.3 Hz, H_a), 5.24 (dt, 1H, $J_{a'c}$= 1.2; $J_{a'b}$= 10.4 Hz, $H_{a'}$), 4.77 (d, 2H, J_{cb}= 5.5 Hz, H_c), 3.91 (s, 3H, H_d), 2.51 (s, 3H, H_i). ^{13}C NMR: δ196.3, 165.3, 162.9, 133.9, 132.7, 132.2, 129.7, 119.9, 118.4, 111.8, 65.5, 56.1, 26.0. IR (CH_2Cl_2): 3088, 3024, 2936, 2854, 1738, 1692, 1612, 1562, 1270, 832 cm^{-1}. EI-MS: m/z= 234 ($M^{+\cdot}$), 219, 205, 193, 179, 177 (base peak). UV-VIS (CH_3OH): λ_{max} = 227.5, 268.0 nm; $\epsilon_{227.5}$= 20 000; $\epsilon_{268.0}$= 15 000 A·$\underline{M}^{-1}$·cm^{-1}.



5′-Acetyl-2′-methoxy 3-butenyl benzoate. In a procedure like that used for the preparation of 4′-butyrylphenyl 3-butenoate[93], this compound was obtained in 75% yield after purification by column chromatography (Davisil-60; 10:90 to 40:60 - EtOAc:hexanes) instead of passage through basic alumina. Eventually, a small amount of oily solid with no clear mp formed in the sample. ^{1}H NMR ($CDCl_3$, 300 MHz): δ8.49 (d, 1H, J_{ig}= 2.4 Hz, H_i), 8.09 (dd, 1H, J_{gi}= 2.4; J_{gf}= 8.0 Hz, H_g), 7.07 (d, 1H, J_{fg}= 8.0 Hz, H_f), 5.99 (m, 1H, H_b), 5.29 (d, 1H, J_{ab}= 18.6 Hz, H_a), 5.23 (d, 1H, $J_{a'b}$= 10.4 Hz, $H_{a'}$), 4.48 (t, 2H, J_{dc}= 6.6 Hz, H_d), 4.07 (s, 3H, H_e), 2.68 (s, 3H, H_j), 2.64 (q, 2H, $J_{cb} \approx J_{cd}$= 7.3 Hz, H_c). ^{13}C NMR: δ196.2, 165.4, 162.7, 134.1, 133.7, 132.5, 129.5, 120.1, 117.3, 111.7, 63.9, 56.0, 32.8, 25.9. IR (CH_2Cl_2): 3075, 2944, 2852, 1730, 1684, 1605, 1503, 839 cm^{-1}. EI-MS: m/z= 248 ($M^{+\cdot}$), 233, 219, 194, 179, 177 (base), 165, 163, 147. UV-VIS (CH_3OH): λ_{max}= ca. 223, 268 nm; ϵ_{223}= 25 000; ϵ_{268}= 16 000 A·$\underline{M}^{-1}$·cm^{-1}.



II. PHOTOLYSIS PROCEDURES

A. Glassware

Solutions for photolysis were prepared and transferred using "Type A" volumetric glassware and glass syringes with stainless steel needles. Photolyses were carried out in 13 x 100 mm pyrex test tubes which were heated with a natural gas/oxygen torch 3 cm from the top and uniformly drawn out and constricted to a 16 cm length.

All glassware used for photokinetic work was especially reserved only for that purpose. It was routinely cleaned by firstly rinsing 3 times with acetone and then boiling 2 - 4 h with a distilled water-Alcanox Detergent solution in a large pyrex jar. After rinsing 5 times with water, it was boiled briefly in clean distilled water. Finally, it was carefully rinsed 5 times and dried at 150°C in an oven reserved exclusively for that purpose.

B. Preparation of Solutions

Stock solutions were prepared by directly measuring weights or volumes into volumetric flasks and diluting to the mark. When necessary, further dilutions were implemented using the same technique. Syringes were used to transfer 2.40 ml aliquots to the photolysis tubes.

C. Degassing

Photolysis tubes were attached to a 10- or 12- port degassing cow through 1-holed #00 rubber stoppers, on line to a vacuum pump. The solutions were then gradually frozen over 10- 15 min by immersion in a liquid nitrogen bath and afterwards exposed to the vacuum for 10 min. After again isolating them from the vacuum, they were allowed to thaw at RT. This cycle was repeated a total of 3 times, whereupon the tubes were once again frozen, evacuated and sealed under vacuum by torch. A mechanical vacuum pump was used in all cases except for the 4'-butyrylphenyl esters, which were sealed under a diffusion pump vacuum.

D. Irradiation

Sealed photolysis tubes were irradiated in parallel in a merry-go-round turntable which revolved around a Hanovia 450 W medium pressure mercury lamp and rested in a large water bath. The lamp was inside of a water-cooled quartz jacket, in turn immersed in a 0.002 M K_2CrO_4-1% K_2CO_3 solution, which served to isolate the 313 nm emission band[120].

E. Analysis

Post-photolysis solutions were analysed using either gas- or high performance liquid- chromatography.

In the former case, either a Varian Aerograph-1400 chromatograph equipped with 15 m Megabore DB-1 or 30 m Megabore DB-Wax columns, or a Varian-3400 chromatograph outfitted with a 15 m Megabore DB-210 column were used, with He carrier gas (flow rates: DB-1: 25, DB-Wax: 30, DB-210: 25 ml/min). The chromatographs were connected to Hewlett-Packard -3392A or -3393A integrating recorders. On-column injection and flame ionisation detectors employing H_2 and compressed air were used at all times. Individual G.C. analysis conditions can be found in Table 13 (vide infra) and with the separate experiments in the Appendix.

In the later instance, a system composed of a Beckman/Altex 332 Programable Gradient Controller, 2 Beckman 110A Solvent Pumps, a Perkin-Elmer LC 75 Ultraviolett-Visible Detector, a DuPont 860 Column Compartment and an Hewlett-Packard 3380A integrating recorder was used with either Altex-25 cm Ultrasphere-ODS Octyl Reverse Phase or Rainin Dynamax Microsorb-25 cm Phenyl Reverse Phase columns.

F. Techniques for 4'-Acylphenyl 3-Butenoate Esters

The instability of these compounds in solution necessitated that the preparation of their photolysis- or calibration- solutions, degassing, irradiation, and analyses be carried out without interruption. The solutions were also kept at 0°C or lower during and after photolysis. Any deviation from these protocol resulted in the partial isomerisation of the photosubstrate and photoproduct. Comparison of pre- and post- irradiation HPLC chromatograms revealed that, within experimental error, no decomposition occurred during photolysis. As an additional precaution, fresh batches of each ester were prepared immediately prior to photolysis or instrument calibration.

III. TECHNIQUES AND CALCULATIONS

A. Stern-Volmer Quenching

In a typical experiment, a 10 ml stock solution of ketone substrate and appropriate internal standard was prepared and 1 ml aliquots were pipetted into a series of 5 ml volumetric flasks. To these were added varying amounts of quencher stock solution and the flasks were diluted to the mark. After irradiation, the ratio of photoproduct concentration in an unquenched solution to that in a given quenched solution was equal to the quantum yield ratio. A plot of Φ^o/Φ against quencher concentration[75] thus yielded a straight line with slope of $k_q\tau$ and intercept of 1.

B. Reciprocal Quantum Yield Versus Ketone Concentration

Varying amounts of a photosubstrate stock solution were added to 1 ml aliquots from an internal standard stock solution and the resulting solutions diluted to 5 ml. In a kinetic paradigm similar to the Stern-Volmer case, a plot of reciprocal quantum yield against ketone concentration gave a straight line with slope equal to $k_{inter}/(k_r P)$ and intercept equal to $1/\Phi_{LIM} = 1/P(1 + k_d/k_r)$, where k_{inter} was the rate constant for ground state quenching[50,81] by both the α,β- and β,γ-unsaturated isomers of the ketone and Φ_{LIM} was the quantum yield for Type II cleavage in the absence of this effect.

C. Quantum Yield Versus Additive Concentration

Varying amounts of an additive stock solution were added to 1 ml aliquots from a photosubstrate-internal standard stock solution in 5 ml volumetric flasks.

D. Photoproduct Concentration

The concentration of the appropriate acetophenone photoproduct, AP' was determined by comparison of its area on the integrating recorder to that of an internal standard present in the photolysis solution in known concentration. The concentration of the photoproduct is thus described by Equation 17, where A_i's represent the relevent integrator areas and R.F., the response factor, is the area/mole ratio of the

$$[AP'] = (A_{pdct}/A_{std}) \times [standard] \times R.F. \qquad (17)$$

standard relative to that of the photoproduct. GC- and HPLC- response factors were assayed from solutions of known concentrations under identical analysis conditions. These values on the pertinent experimental equipment are summarised in Table 13.

Table 13. Gas Chromatographic- and HPLC- Photoproduct Response Factors

Standard/Product	$\frac{(\text{Area/mole})_{std}}{(\text{Area/mole})_{pdct}}$	# Trials
hexadecane/AP[a]	2.20±0.04	3
^{n}octyl benzoate/$\underline{p}$CO$_2$allylAP[b]	1.62±0.03	3
^{n}octyl benzoate/$\underline{p}$CO$_2$prenylAP[c]	1.38±0.02	1
^{n}heptyl benzoate/$\underline{p}$CO$_2$butenylAP[d]	1.60±0.02	1
^{n}butyl benzoate/$\underline{p}$OAcAP[e]	1.53±0.04	4
^{n}heptyl benzoate/$\underline{p}$OAcAP[f]	1.62±0.01	1
ethyl benzoate/$\underline{p}$ObutenoateAP[g]	0.127±0.001	1
^{n}propyl benzoate/$\underline{p}$ObutenoateAP[h]	0.118±0.001	1
^{n}octyl benzoate/$\underline{p}$OpentenoateAP[i]	1.72±0.05	4

[a]: acetophenone (DB-Wax column (110°)). [b]: 4'-acetyl allyl benzoate (DB-210 GC column; 80° (2 min), then to 150° (50°/min)). [c]: 4'-acetyl prenyl benzoate (analysis same as $\underline{p}$CO$_2$allylAP). [d]: 4'-acetyl 3-butenyl benzoate (DB-210 GC column; 80° (2 min), then to 160° (50°/min)). [e]: 4'-acetylphenyl acetate (DB-1 GC column (110°)). [f]: with $\underline{p}$OAcVP-benzene Stern-Volmer experiments (DB-210 GC column; 80° (2 min), then to 140° (50°/min)). [g]: 4'-acetylphenyl 3-butenoate; Stern-Volmer experiments (ODS-octyl reverse phase HPLC column; CH_3OH-H_2O mobile phase; 250 nm detection). [h]: reciprocal quantum yield experiments (phenyl reverse phase HPLC column; CH_3CN-H_2O mobile phase; 250 nm detection). [i]: 4'-acetylphenyl 4-pentenoate (DB-1 GC column (145°)).

E. Quantum Yields

The absolute quantum yields for the formation of acetophenone photoproducts at 313 nm, from the photosubstrates studied, AP', were determined by parallel irradiation of valerophenone actinometer solutions in benzene[16]. The quantum yield of valerophenone under the current conditions, Φ_{II}^{VP} is known to follow the simple dependence on valerophenone concentration described in Equation 18[13].

$$\Phi_{II}^{VP} = 0.30[VP] + 0.30 \tag{18}$$

The unknown quantum yield, Φ_{II}, is obtained through Equation 19, where AP stands for simple acetophenone. The factor $(1\text{-}T_{VP})/(1\text{-}T)$, where T^{VP} and T were the optical transmissions of valeropheone and the photosubstrate respectively, is a correction factor allowing for

$$\Phi_{II} = \Phi_{II}^{VP} \cdot [AP']/[AP] \cdot (1\text{-}T^{VP})/(1\text{-}T) \tag{19}$$

incomplete light absorption by valerophenone or the photosubstrate. The acetophenoen photoproduct under analysis is denoted by AP'. Corrections for this phenomenon were necessary in the quantum yield measurements from the Φ_{II}^{-1} versus [photosubstrate] experiment where photosubstrate concentration was 0.02 M̲ or lower and all of the quantum yields from the Φ_{II} versus [pyridine] experiment.

IV. SPECTRA

A. Proton NMR Spectra

Spectra of synthetic intermediates were usually recorded with a Varian T-60 Continuous Wave Spectrometer in $CDCl_3$ previously stored over anhydrous K_2CO_3 with tetramethylsilane reference absorption at $\delta 0.0$. Photsubstrate spectra were taken with 250 MHz Bruker- or 300 MHz Varian/Gemini- Fourier Transform Spectrometers. In those cases, the ^1H-signal from the solvent provided the appropriate reference signal at $\delta 7.24$.

B. Carbon NMR Spectra

Carbon-13 spectra were recorded on the Varian/Gemini Spectrometer in $CDCl_3$, referred to the $CDCl_3$ signal at $\delta 77.0$.

C. Ultraviolett - Visible Spectra

Spectra were recorded on a Shimadzu UV-VIS Recording UV-16 Spectrophotometer in 1 cm quartz Beckman cells. Solvents used were photolysis methanol or Mallinckrodt Specrophotometric Grade ^{n}heptane. Background correction was implemented by running a blank of the same cell filled with pure solvent.

D. Infrared Spectra

Spectra were recorded in a KBr solution cell with spectrograde CCl_4, $CHCl_3$ or CH_2Cl_2 or as KBr pellets on a Perkin-Elmer Model 237 B Grating Spectrometer or a Nicolet IR/42 Fourier Transform Spectrometer controlled by a Dell System 2000 - IBM/30S Upgrade Unit computer and outputted to a Hewlett-Packard ColorPro Plotter. On the latter instrument, the solution spectra were blanked by the pure solvent. Spectra were calibrated to the 1603 cm^{-1} absorption of polystyrene[121].

E. Mass Spectra

Mass spectra were recorded on a Finnigan 4000 GC/MS system using the direct inlet mode by Kenneth Rehder or Ernest Oliver.

F. Phosphorescence Spectra

Phosphorescence spectra were recorded from ca. 10^{-4} $\underline{M}$ solutions at 313 nm excitation wavelength at 77°K in 5 mm diameter pyrex NMR tubes. A Perkin-Elmer MPF-44A Fluorescence Spectrometer, scanning at a rate of 120 nm/min and filtered by a chopper rotating at a rate of 1 700 cycles/sec, was outputted to a Hewlett-Packard 3393A integrating recorder. Phosphorescence grade solvents were kindly provided by Dr. J. DeFrancesco.

V. NMR TUBE IRRADIATIONS

A. Sample Preparation

A pyrex WG-XR-55 NMR tube was drawn out and constricted with a torch. Approximately 0.2 ml of the appropriate concentration of ketone, usually in methanol-d_4 containing traces of benzene-d_6 (to lessen the rate of expansion of the solutions upon thawing), was added to this through a syringe. The top of the tube was fitted tightly with the wider end of a small rubber septum and several small, fine needles were inserted partially into the tube through the septum. The top of the septum was pushed into the hole of a rubber stopper on a vacuum cow. Contact with the vacuum line was maintained through the needles. The solutions were then degassed and sealed in vacuum as previously described.

B. Sample Irradiation and Monitoring

Degassed and vacuum-sealed NMR tubes were irradiated directly outside of a Hanovia medium pressure mercury lamp outfitted with a quartz water jacket and a pyrex sleeve. The irradiations were intermittantly stopped and the ^1H NMR spectra recorded on the 250 MHz Bruker instrument.

C. Individual Runs

4′-Acetyl allyl benzoate/benzene-d_6. A 0.03 M solution was degassed by bubbling with Ar gas and irradiated up to 6.5 h. Spectra recorded throughout the irradiation indicated the appearance of minor signals at δ5.88 (dd), 4.44 (dd) and 4.06 (dq) as well as δ1.9 (s), 1.55 (d), and 1.52 (d?). The vinyligous and allylic signals of the starting ketone remained essentially unchanged. A large amount of insoluable material was present on top of the solution at the conclusion of the experiment. Analysis of the photolysis solution by analytical t.l.c. revealed only traces of the starting material in addition to large amounts of non-eluting material.

4′-Acetyl allyl benzoate/methanol-d_4. A 0.055 M solution, degassed and sealed under vacuum, was irradiated up to 15 h. Intermittant spectra revealed the gradual disappearance of the acetyl group in the starting material and the appearance of aromatic doublets at δ7.29, 7.52, 7.77 and 7.88, as well as other signals at δ1.48, 1.52, 1.62 and 2.19. The signals from the allylic tether remained essentially unchanged. A large amount of insoluable material was present at the end of the photolysis.

4′-Acetyl 3-butenyl benzoate/methanol-d_4. A 0.044 M solution, degassed and sealed under vacuum, was irradiated up to 13 h. Intermittant spectra showed the build up of signals in the δ0.2 region, concomittant with the formation of a white, insoluable material.

4′-Acetylphenyl 3-butenoate/methanol-d_4. A 0.03 M solution of freshly prepared 4′-actylphenyl 3-butenoate, degassed and sealed under vacuum, was irradiated for 12 h. Spectra recorded at intervals of 1, 4 and 12 h indicated the replacement of the aromatic peaks in the starting material with peaks at δ7.81 (d) and 6.78 (d) along with an increase in the complexity of the peaks in the δ5.8-6.0 and 5.0-5.3 regions with irradiation time. Analysis of the photolysis mixture by GC (DB-1 column, column temperature= 120°C) showed only the starting material and slight traces of broad peaks at higher retention times.

5′-Acetyl-2′-methoxy allyl benzoate/methanol-d_4. A 0.0029 M solution, degassed and sealed under vacuum, was irradiated up to ca. 100 h. Spectra recorded at 4, 25 and 100 h showed the gradual disappearance of the starting ketone, concomittant with the appearance of miscellaneous peaks in the δ0.9 to 2.5 region. An insoluable material was present in solution at the conclusion of the experiment.

5′-Acetyl-2′-methoxy 3-butenyl benzoate/methanol-d_4. A 0.0030 M solution, degassed and sealed under vacuum, was irradiated up to 100 h. Spectra recorded at 4 and 25 h showed the gradual disappearance of the starting material, concomittant with the appearance of peaks in the δ1.0 to 2.3 region. A film was present on the surface of the solution by the end of the irradiation.

VI. MOLECULAR MECHANICS CALCULATIONS

Molecular mechanics calculations were implemented on a IBM PC/XT computer with an enhanced graphics adapter. The MMX87 program, distributed by Serena Software, Bloomington, Indiana/ 47402 was used. The input files were generated by the STRPI/MIOSTR subroutine and

SERENA configuration file and were submitted for processing by the MAKESTM subroutine. Output structures were created by the MIOGRFX subroutine. The MMX87 program featured open shell enhanced PI subroutines and improved torsional constants for esters (relative to the older, MMPI program). As well, it specified only one lone pair of electrons for ester oxygens.

The lowest energy conformations of 4'-acetylphenyl 3-butenoate and 4'-acetyl allyl benzoate were determined from restricted Hartree-Foch calculations on their ground state, singlet STRPI/MIOSTR structures. All oxygen atoms and sp^2-hybrid carbon atoms were declared PI atoms and 14- and 12- PI electrons were alotted to each, respectively.

The ester twisting calculations were implemented through the introduction of dihedral angle drives about the C-C-O-C dihedral angle of the ester bond β to the aromatic ring. The STRPI/MIOSTR input structures were otherwise unchanged from before. The angle drives were specified to rotate from 180° (trans-coplanar) to 0° (cis-coplanar) in 10° increments. Thus, the otherwise lowest energy conformations for a total of 19 structures for each were calculated in the second set of experiments.

APPENDIX

Table 14. **Quenching of Acetophenone Formation from 4'-Valeryl Allyl Benzoate with 2,5-Dimethyl-2,4-Hexadiene in Benzene**

Run #1:

Photosubstrate:

[ketone]= 0.030 M
wavelength= 313 nm
temperature: ambient
column: DB-210; 80° for 2 min, then to 150° at 50°/min; peak width= 2.0.
internal standard: n-octyl benzoate
[standard]= 0.0031 M

$k_q\tau = 52 \pm 2\ M^{-1}$ $\Phi_{II} = 0.21$

$10^3 x[Q]$, M	AP'/standard area ratio	$10^3 x[AP']$, M	Φ^o/Φ
0	0.381	1.90	1.00
2.90	0.287	1.43	1.34
5.80	0.265	1.32	1.45
11.6	0.214	1.07	1.79
20.4	0.173	0.863	2.22
30.6	0.1376	0.686	2.80
40.8	0.1116	0.554	3.47

Actinometer:

[VP]= 0.17 M
wavelength= 313 nm
temperature: ambient
internal standard: hexadecane
[standard]= 0.020 M

AP/standard area ratio	$10^3 x[AP]$, M	$10^3 x I_a$
0.706	3.0_6	8.7_5

Table 14 (cont'd.)

Run #2:

Photosubstrate:
[ketone]= 0.030 M
wavelength= 313 nm
temperature= ambient
column: see Run #1
internal standard: n-octyl benzoate
[standard]= 0.0033 M

$k_q\tau$ = 58±4 M^{-1} Φ_{II} = 0.16[b]

10^3x[Q], M	AP'/standard area ratio	10^3x[AP'], M	Φ^o/Φ
0	0.208	1.02	1.00
3.04	0.176	0.862	1.18
6.08	0.134	0.654	1.56
12.16	0.128	0.626	1.63
20.8	0.0929	0.455	2.24
31.1	0.0729	0.357	2.86

Actinometer:
[VP]= 0.103 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.010 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.0932	6.2_6	6.2_6

Table 15. Quantum Yield of Acetophenone Formation from 4'-Valeryl Prenyl Benzoate in Benzene

Photosubstrate:
[ketone]= 0.029 M
wavelength= 313 nm
temperature= ambient
column= DB-210; 80° for 3 min, then to 150° at 50°/min, then hold at 150° for 10 min; peak width= 2.0 until 14 min, then peak width= 32.
internal standard: n-octyl benzoate
[standard]= 0.0047 M

Φ_{II}= 0.247

AP'/standard area ratio	10^3x[AP'], M
0.3220	0.0211

Actinometer:
[VP]= 0.111 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.010 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.128	2.9_0	8.7_0

Table 16. **Quenching of Acetophenone Formation from 4'-Valeryl 3-Butenyl Benzoate with 2,5-Dimethyl-2,4-Hexadiene in Benzene**

Run #1:

Photosubstrate:
[ketone]= 0.030 M
wavelength= 313 nm
temperature= ambient
column: DB-210; 80° for 2 min, then to 160° at 50°/min, then hold at 160° for 8 min; peak width= 2.0 up to 8 min, then peak width= 16.
internal standard: n-octyl benzoate
[standard]= 0.0015 M

$k_q\tau$= 60±2 M^{-1} Φ_{II}= 0.18

10^3x[Q], M	AP'/standard area ratio	10^3x[AP'], M	Φ^o/Φ
0	1.18	2.26	1.00
1.06	1.071	2.05	1.10
2.12	0.975	1.86	1.22
4.23	0.89	1.70	1.33
10.6	0.720	1.38	1.64
21.2	0.519	0.992	2.28

Actinometer:
[VP]= 0.10 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.010 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.188	4.14	$12._5$

Table 16 (cont'd.)

Run #2:

Photosubstrate:
[ketone]= 0.030 M
wavelength= 313 nm
temperature= ambient
column: see Run #1
internal standard: n-octyl benzoate
[standard]= 0.0015 M

$k_q\tau$= 62±2 M^{-1} Φ_{II}= 0.18

10^3x[Q], M	AP'/standard area ratio	10^3x[AP'], M	Φ^o/Φ
0	1.04	2.04	1.00
2.02	0.801	1.56	1.30
4.03	0.771	1.50	1.35
8.06	0.648	1.26	1.60
20.3	0.464	0.905	2.24

Actinometer:
[VP]= 0.10 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.0100 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.170	3.7_4	$11._3$

Table 17. Quenching of Acetophenone Formation from 4'-Valerylphenyl Acetate with 2,5-Dimethyl-2,4-Hexadiene in Benzene

Run #1:

Photosubstrate:
[ketone]= 0.032 M
wavelength= 313 nm
temperature= ambient
column= DB-210; 80° for 2 min, then to 140° at 50°/min, then held at 140° for 15 min; peak width= 2.0.
internal standard: n-heptyl benzoate
[standard]= 0.0020 M

$k_q\tau$= 76±2 M^{-1} Φ_{II}= 0.269

10^3x[Q], M	AP'/standard area ratio	10^3x[AP'], M	Φ^o/Φ
0	0.430	1.41	1.00
2.00	0.356	1.19	1.19
5.99	0.291	0.973	1.45
12.0	0.225	0.753	1.87
16.0	0.192	0.643	2.19

Actinometer:
[VP]= 0.11 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.011 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.073	1.7	5.2

Table 17 (cont'd.)

Run #2:

Photosubstrate:
[**ketone**]= 0.040 M
wavelength= 313 **nm**
temperature= **ambient**
column: **see Run #1**
internal standard: n-heptyl benzoate
[**standard**]= 0.0020 M

$k_q\tau$= 77±2 M^{-1} Φ_{II}= 0.28

10^3x[Q], M	AP'/standard area ratio	10^3x[AP'], M	Φ^o/Φ
0	0.54	1.8	1.0
4.00	0.3585	1.19	1.5_1
8.00	0.326	1.08	1.6_7
12.0	0.259	0.860	2.0_9
16.0	0.222	0.737	2.4_4
20.0	0.201	0.667	2.7_7
36.0	0.140	0.465	3.8_7
40.0	0.130	0.432	4.1_7

Actinometer:
[**VP**]= **0.10** M
wavelength= **313 nm**
temperature= **ambient**
internal standard: hexadecane
[**standard**]= **0.010** M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.096	2.1	6.4

Table 18. Dependence of Quantum Yield of Acetophenone Formation from 4'-Valerylphenyl Acetate on Concentration of Pyridine in Benzene

Photosubstrate:
[ketone]= 0.031 M
wavelength= 313 nm
temperature= ambient
column: DB-1, 110°; peak width= 0.16.
internal standard: n-butyl benzoate
[standard]= 0.00120 M

Φ_{II}^{o}= 0.27 (from Table 17, Run #1) Φ_{MAX}= 0.756

$[C_6H_5N]$, M	AP'/standard area ratio	10^4x[AP'], M	Φ_{II}
0.119	0.218	4.00	0.457
0.237	0.285	5.23	0.597
0.356	0.320	5.88	0.670
0.474	0.338	6.21	0.706
0.990	0.3612	6.63	0.756
1.98	0.344	6.32	0.720
2.97	0.322	5.91	0.695

Actinometer:
[VP]= 0.077 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.0936 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.0137	2.8_3	8.7_6

Table 19. **Quenching of Acetophenone Formation from 4'-Valerylphenyl Acetate with 2,5-Dimethyl-2,4-Hexadiene in 4:1-Methanol:Benzene**

Run #1:

Photosubstrate:
[ketone]= 0.030 M
wavelength= 313 nm
temperature= ambient
column= see Table 18, Run #1.
internal standard: n-butyl benzoate
[standard]= 0.0013 M

$k_q\tau$= 188±6 M^{-1} Φ_{II}= 0.82

10^4x[Q], M	AP'/standard area ratio	10^3x[AP'], M	Φ^o/Φ
0	0.76_0	1.4_4	1.0
8.31	0.613	1.18	1.2_2
16.6	0.537	1.04	1.3_9
24.9	0.481	0.927	1.5_5
41.6	0.3938	0.759	1.8_9
83.1	0.297	0.573	2.5_1
124.7	0.216	0.417	3.4_5

Actinometer:
[VP]= 0.077 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.0094 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.028	0.57_7	0.17_8

Table 19, (cont'd.)

Run #2:

Photosubstrate:
[ketone]- 0.030 M
wavelength- 313 nm
temperature- ambient
column: see Table 18, Run #1.
internal standard: n-butyl benzoate
[standard]- 0.0017 M

Φ_{II}- 0.86

AP'/standard area ratio	10^3x[AP'], M
0.62	1.63

Actinometer:
[VP]- 0.11 M
wavelength- 313 nm
temperature- ambient
internal standard: hexadecane
[standard]- 0.010 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.026	0.59	1.79

Table 20. **Quenching of Acetophenone Formation from 4'-Butyrylphenyl Acetate with 2,5-Dimethyl-2,4-Hexadiene in 4:1-Methanol:Benzene**

Run #1:

Photosubstrate:
[ketone]= 0.030 M
wavelength= 313 nm
temperature= ambient
column: see Table 18, Run #1.
internal standard: n-butyl benzoate
[standard]= 0.0016 M

$k_q\tau$= 2 300±100 M^{-1} Φ_{II}= 0.55

10^5x[Q], M	[AP']/standard area ratio	10^3x[AP'], M	Φ^o/Φ
0	1.15	2.74	1.00
5.18	0.9584	2.27	1.20
10.4	0.894	2.12	1.29
15.6	0.756	1.79	1.53
20.7	0.705	1.69	1.64
31.1	0.661	1.57	1.75
41.4	0.547	1.30	2.10
51.8	0.524	1.24	2.20
62.2	0.463	1.10	2.49

Actinometer:
[VP]= 0.10 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.0092 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.081	1.6	5.0

Table 20 (cont'd.)

Run #2:

Photosubstrate:
[ketone]= 0.033 M
wavelength= 313 nm
temperature= ambient
column: see Table 18, Run #1.
internal standard: n-butyl benzoate
[standard]= 0.0016 M

$k_q\tau$= 2 600±200 M^{-1} Φ_{II}= 0.68

10^4x[Q], M	AP'/standard area ratio	10^3x[AP'], M	Φ^o/Φ
0	1.241	3.00	1.00
1.15	0.90	2.1_7	1.3_8
1.72	0.79	1.9_1	1.5_7
2.30	0.597	1.44	1.68
3.44	0.5456	1.32	1.83
4.59	0.4423	1.07	2.26

Actinometer:
[VP]= 0.10 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.0092 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.071	1.4	4.3

Table 21. Quenching of Acetophenone Formation from 4'-Butyrylphenyl 3-Butenoate with 2,5-Dimethyl-2,4-Hexadiene in 4:1-Methanol:Benzene

Run #1:

Photosubstrate:
[ketone]= 0.030 M (containing 4.1% crotonate isomer)
wavelength= 313 nm
temperature= 0°C
column: Altex-Ultrasphere-ODS octyl reverse phase HPLC column; 4.6 mm diameter x 25 cm length; UV detection at 250 nm; solvent gradient program (%methanol in water; flow rate= 1.0 ml/min): 62%, then at 10 min to 90% over 2 min, then at 15 min to 95% over 0.5 min, then at 15.5 min to 62% over 3.5 min, stayed at 62% untill 26 min; 35°C.
internal standard: ethyl benzoate
[standard]= 0.019 M

$k_q\tau$= 390 M^{-1} Φ_{II}= 0.13

10^4x[Q], M	AP'/standard area ratio	10^4x[AP'], M	Φ^o/Φ
1.92	0.1838	4.51	1.08
2.87	0.1762	4.32	1.12
3.83	0.175	4.29	1.13
5.75	0.1637	4.01	1.21
7.66	0.1520	3.73	1.31

Actinometer:
[VP]= 0.11 M
wavelength= 313 nm
temperature= 0°C
internal standard: hexadecane
[standard]= 0.010 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.053	1.2	3.66

Table 21 (cont'd.)

Run #2:

Photosubstrate:
[ketone]= 0.030 $\underline{M}$ (containing 3.9% crotonate isomer)
wavelength= 313 nm
temperature= 0°C
column: see Run #1
internal standard: ethyl benzoate
[standard]= 0.013 $\underline{M}$

$k_q\tau = 420\ \underline{M}^{-1}$ $\Phi_{II} = 0.11$

10^4x[Q], $\underline{M}$	AP'/standard area ratio	10^4x[AP'], $\underline{M}$	Φ^o/Φ
0.00	0.310	4.96	1.00
4.92	0.2608	4.17	1.19
9.84	0.2087	3.34	1.48
14.8	0.183	2.93	1.70
19.7	0.1622	2.60	1.91
29.5	0.137	2.19	2.26
39.5	0.1166	1.87	2.65

Actinometer:
[VP]= 0.11 $\underline{M}$
wavelength= 313 nm
temperature= 0°C
internal standard: hexadecane
[standard]= 0.010 $\underline{M}$

AP/standard area ratio	10^3x[AP], $\underline{M}$	10^3xI_a
0.063	1.4_4	4.3_4

Table 22. **Dependence of Quantum Yield of Acetophenone Formation from 4'-Butyrylphenyl Butenoate on Concentration of Photosubstrate in 4:1-Methanol:Benzene**

Run #1:

Photosubstrate:
[ketone]: see following table
wavelength= 313 nm
temperature= 0°C
column: Dynamax Microsorb-phenyl bonded phase 4.6 x 250 mm reverse phase HPLC column; UV detection at 250 nm; solvent gradient program (% acetonitrile in water; flow rate= 1.0 ml/min): 36%, then at 15 min to 50% over 0.5 min, then at 22 min to 36% over 0.5 min, stayed at 36% untill 28 min; 35°C.
internal standard: n-propyl benzoate
[standard]= 0.0063 M

Φ_{LIM}= 0.1192±0.0009[a]   slope= 62±1 M^{-1} [a]

[Ketone], M	AP'/standard area ratio	10^4x[AP'], M	Φ_{II}	Φ_{II}^{-1}
0.01002	0.8214	5.28	0.104	9.62
0.03008	0.778	5.00	0.0980	10.2
0.04058	0.724	4.65	0.0912	11.0
0.06087	0.6534	4.20	0.0823	12.2
0.08116	0.594	3.82	0.0749	13.4

[a]: Φ_{LIM} is Φ_{II} at infinite dilution, taken from line equation of plot of reciprocal quantum yield versus starting ketone concentration.

Actinometer next page

Table 22, Run #1 (cont'd.)

Actinometer:
[VP]= 0.010 M
wavelength= 313 nm
temperature= 0°C
internal standard: hexadecane
[standard]= 0.00933 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.082	1.6_8	5.1

Table 22 (cont'd.)

Run #2:

Photosubstrate:
[ketone]: see following table
wavelength= 313 nm
temperature= 0°C
column: see Run #1
internal standard: n-propyl benzoate
[standard]= 0.0061 M

Φ_{LIM}= 0.119±0.001[a] slope= 76±3 M^{-1} [a]

[Ketone], M	AP'/standard area ratio	10^4x[AP'], M	Φ_{II}	Φ_{II}^{-1}
0.01018	1.046	7.58	0.102	9.80
0.02036	1.008	7.30	0.0984	10.2
0.03054	0.975	7.06	0.0952	10.5
0.04024	0.908	6.58	0.0887	11.3
0.06035	0.784	5.68	0.0766	13.1
0.08047	0.706	5.12	0.0690	14.5

[a]: Φ_{LIM} and slope calculated as in Run #1.

Actinometer:
[VP]= 0.10 M
wavelength= 313 nm
temperature= 0°C
standard= hexadecane
[standard]= 0.0032 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.035_2	0.24_5	0.74_1

Table 23. Quenching of Acetophenone Formation from 4'-Valerylphenyl Acetate with Methyl Crotonate in 4:1-Methanol:Benzene[a]

Run #1:

Photosubstrate:
[ketone]= 0.030 M
wavelength= 313 nm
temperature= ambient
column: see Table 18, Run #1.
internal standard: n-butyl benzoate
[standard]= 0.0013 M

$k_q\tau = 33 \pm 3$ M^{-1}

$\Phi_{II} = 0.87$

10^3x[Q], M	AP'/standard area ratio	10^3x[AP'], M	Φ^o/Φ
0	1.77	3.37	1.00
3.20	1.66	3.31	1.07
5.34	1.495	2.98	1.18
10.7	1.32	2.63	1.34

Actinometer:
[VP]= 0.11 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.010 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.057	1.3	3.9

Table 23 (cont'd.)

Run #2:

Photosubstrate:
[ketone]= 0.030 M
wavelength= 313 nm
temperature= ambient
column: see Table 18, Run #1.
internal standard: n-butyl benzoate
[standard]= 0.0013 M

$k_q\tau = 33\pm2\ \underline{M}^{-1}$

10^3x[Q], M	AP'/standard area ratio	10^3x[AP'], M	Φ^o/Φ
0	1.11	1.89	1.00
3.04	0.905	1.78	1.07
6.08	0.84	1.64	1.15
15.2	0.708	1.39	1.36
18.2	0.621	1.21	1.55
30.4	0.478	0.936	2.01

Actinometer:
none

Table 24. Quenching of Acetophenone Formation from 4'-Butyrylphenyl 4-Pentenoate with 2,5-Dimethyl-2,4-Hexadiene in 4:1-Methanol:Benzene[a]

Run #1:

Photosubstrate:
[ketone]= 0.030 M
wavelength= 313 nm
temperature= ambient
column: DB-1; 145°
internal standard: n-octyl benzoate
[standard]= 0.0010 M

$k_q\tau$= 2 300±200 M^{-1} Φ_{II}= 0.37

10^5x[Q], M	AP'/standard area ratio	10^4x[AP'], M	Φ^o/Φ
0	0.409	7.03	1.00
7.91	0.330	5.67	1.24
15.8	0.2616	4.50	1.56
23.7	0.245	4.21	1.67
31.7	0.206	3.54	1.99
47.5	0.1840	3.17	2.22
63.3	0.167	2.87	2.45

Actinometer:
[VP]= 0.10 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.0093 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.031	0.64	1.93

Table 24 (cont'd.)

Run #2:

Photosubstrate:
[ketone]= 0.030 M
wavelength= 313 nm
temperature= ambient
column: see Run #1
internal standard: n-octyl benzoate
[standard]= 0.00090 M

$k_q\tau$= 2400±100 M^{-1} Φ_{II}= 0.42

10^5x[Q], M	AP'/standard area ratio	10^4x[AP'], M	Φ^o/Φ
0	0.579	8.52	1.00
7.40	0.4307	6.67	1.32
22.2	0.380	5.85	1.50
29.6	0.324	5.00	1.76
44.4	0.269	4.14	2.12
59.2	0.228	3.51	2.50

Actinometer:
[VP]= 0.10 M
wavelength= 313 nm
temperature= ambient
internal standard: hexadecane
[standard]= 0.00316 M

AP/standard area ratio	10^3x[AP], M	10^3xI_a
0.097	0.67	2.0

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