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SUBSTITUENT AND STRUCTURAL EFFECTS ON THE PHOTOCHEMISTRY OF BICYCLIC βγ-UNSATURATED KETONES.

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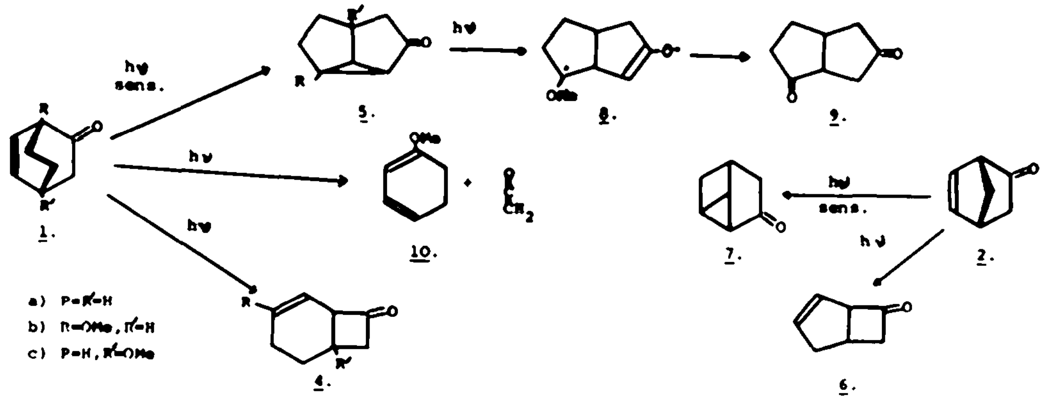
Abstract - The direct and sensitized irradiations of the βγ-unsaturated ketones 1(a-c) and 2 have been investigated. 1a, 1c and 2, on direct irradiation give rise to ODPM rearrangement in addition to the expected [1,3]-acyl shift. These represent the first examples of ODPM rearrangements arising from some state other than $T_1(\pi-\pi^*)$. [1,3]-Acyl shifts observed in the sensitized reactions can involve direct absorption of light and singlet energy transfer from acetone in addition to population of the $T_2(n-\pi^*)$ state.

During the past twenty years, the photochemistry of βγ-unsaturated ketones has excited a great deal of interest, which has largely focussed on the two unique acyl-migration reactions, the [1,3]-acyl shift and the [1,2]-acyl shift or oxadi-π-methane (ODPM) rearrangement. The earlier literature on these reactions has been extensively reviewed[1], and the more recent mechanistic work has been the subject of a critical article[2]. Some years ago we initiated a study of substituent and structural effects on the photochemistry of βγ-enones, choosing for this purpose the bicyclo[2,2,2]oct-5-en-2-one system (1), because preliminary results were available for the parent enone (1a)[3], and because a range of substituted examples were readily available from aromatic starting materials[4]. Effects associated with ring-size and conformation were also of interest, and norbornenone(2), on which considerable data was available[5], and the bicyclo[3,2,1]oct-6-en-2-one (3) were included in the planned study. The present paper presents some of our work with the enones 1 and 2, the basic features of which are outlined in Scheme I. Preliminary reports of some of these results have appeared[6].

Scheme I



RESULTS

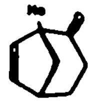
A. Direct Irradiation. Irradiation (300 nm) of **1b** and **1c** in a variety of solvents gave results qualitatively very similar to those observed for **1a**[3], the expected [1,3]-acyl-shift product being accompanied by volatile fragmentation products derived from 1-methoxy-1,3-cyclohexadiene (**10b**)*. This group of products became more important at longer reaction times, in accord with their observed formation as the only photoproducts from irradiation of **4b** and **4c**$^{cf.3}$. This trend is recorded in **Table II** which lists the relative GLC peak areas of **4b** ($A_{1,3}$) and the combined fragmentation products (A_F) against reaction time.

An important difference from the reported photochemistry of **1a** was observed on direct irradiation of **1c**, when a small but reproducible yield of the ODPM product (**5c**) was formed. Very careful reinvestigation of the direct irradiation of **1a** and **2** revealed similar behaviour. In none of the three cases was the anomalous ODPM product selectively quenched by piperylene or 1,3-cyclohexadiene. Quantum yields for the direct irradiation and quenching experiments are listed in **Table I**.

Table I. Quantum Yields[a] for Direct Irradiations.

Enone	Φ_K	$\Phi_{1,3}$	Φ_{ODPM}	Φ_F[b]
1a	-	0.6	0.03	-
1b[c]	0.8	0.5	-	0.2
1b[d]	0.8	0.5	-	0.2
1b[e]	0.5	-	-	-
1c	0.85	0.66[f]	0.056[f]	-
1c[g]	-	0.54	0.024	-
1c[h]	-	0.21	0.01	-
1c[i]	-	0.14	0.008	-
2	0.6	0.3	0.004	-

[a] Ketones (~0.5M) irradiated (300nm). Results refer to ~10% conversion and are the average of at least two runs. GLC analyses were the average of at least three injections: estimated error ±10%. In the cases of 1a and 2 analysis was by a combination of GLC and solution ir: the error was probably >10%. Actinometry was by potassium ferrioxalate[14] or by benzophenone-benhydrol[10]. [b] Φ_F refers to the quantum yield of combined fragmentation products. [c] Heptane. [d] Benzene (254nm). [e] Methanol. [f] Value obtained by extrapolation to zero conversion. [g] Benzene (14% conversion). [h] Benzene (0.28M piperylene). [i] Benzene (1.47M piperylene).



3.

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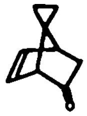
12.



13.

B. Sensitized Irradiation. Irradiation of **1b** in acetone (254 or 300 nm), or in benzene containing acetophenone (350 nm) gave the expected ODPM product (**5b**) in only very low yield. The major product was bicyclo[3,3,0]octan-2,7-dione (**9**) which was isolated in good chemical yield. This reaction has obvious synthetic potential, and examples of its use have appeared[9] since the original report[6a]. Irradiation of **5b** in acetone solution yielded **9** as the only product.

Accompanying **5b** and **9** in the sensitized irradiation of **1b** were **4b** and the same fragmentation products observed on direct irradiation. **1c** on sensitized irradiation gave **5c** as the major product, as expected. Also formed in low yield were the [1,3]-acyl shift product (**4c**) and fragmentation products. Similar behaviour was exhibited by **1a**. The quantum yields for these sensitized reactions are listed in **Table III**. In the case of **1b** the photoreaction was followed

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*Presumably 2,3-dihydroanisole is the first formed photofragmentation product. A preliminary study[7] revealed that this diene on irradiation gave 2,5-dihydroanisole and anisole, the process being more efficient in presence of the enone **1b**. In methanol, cyclohex-2-enone and cyclohex-3-enone, presumably arising from hydrolysis by traces of water[8] were also present together with less volatile addition compounds.

by the analysis of aliquots. The results are illustrated in <u>**Figure 1**</u>. A notable feature is the delay in the build-up of the ODPM products (**5e** and **9**), behaviour very reminiscent of that reported[5d.] for norbornenone (**2**). This effect was found to be concentration-dependent, and was not apparent at concentrations of **1b** of less than 0.025M.

<u>**Table II**</u>. Fragmentation Yield as a Function of Time.

Time(min)	$A_{1,3}/A_F$
4	2.2
6	2.3
8	2.2
10	2.1
20	1.9
45	1.5
120	1.0

<u>**Table III**</u>. Quantum Yields for Sensitized Reactions.

Enone	Sensitizer	Φ_{-K}	Φ_{ODPM}	$\Phi_{1,3}$
1a	Acetone^a	0.3	0.19	0.08
1b	Acetone^a	0.3	0.7	0.07^b
1b	Acetophenone^c	0.034	0.016	0.001
1e	Acetone^a	0.42	0.18	0.045
2^d	Acetone^a	0.4	0.16	0.18
2^e	Acetone^a	0.48^e	0.11	0.16
2^d	Acetophenone	0.14	0.13	0.013
2^d	Benzophenone	0.071	0.042	0.006

^{a}Solvent:300nm. ^{b}Considerable fragmentation observed: $_F$ 0.08. ^{c}0.057M in benzene: 350nm. ^{d}Data from ref.5d. ^{e}This study.

Qualitative quenching experiments revealed that under conditions of either acetone- or acetophenone-sensitized irradiation of **1a–e** and **2**, piperylene and 1,3-cyclohexadiene (in concentrations of ~0.01M.) markedly lowered the ratio $\Phi_{1,3}/\Phi_{ODPM}$. In addition, the use of soda-glass in place of pyrex tubes in the acetophenone-sensitized reactions of **1b** and **2** produced a selective reduction in the yield of [1,3]-acyl shift product. Quantitative quenching data in acetone for the enones **1b** and **1e** are presented in <u>**Table IV**</u> and illustrated for **1e** in <u>**Figure 2**</u>.

<u>**Table IV**</u>: Quenching of Acetone-Sensitized Reactions of **1b** and **1e**.

$[Q]^a$ (10^3M)	Φ_o/Φ(-K)	Φ_o/Φ(1,3)	Φ_o/Φ(ODPM)^b	$[Q]^c$ (10^3M)	Φ_o/Φ(1,3)	Φ_o/Φ(ODPM)
0	1	1	1	0	1	1
2.33	1.26	-	1.62	1.06	1.00	1.66
4.66	1.59	-	3.44	2.11	0.85	2.08
6.99	2.09	-	-	3.18	1.05	2.53
8.20	1.86	-	8.70	4.24	1.11	3.40
11.65	2.09	1.05	-	5.27	1.00	4.86
30.00	1.89	-	-	6.37	1.31	6.55
49.00	1.96	0.98	-	7.43	1.11	7.52

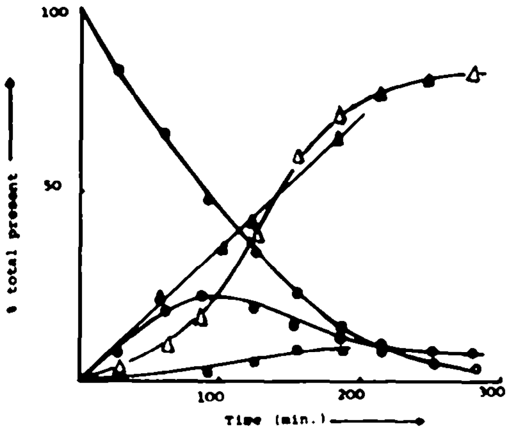
^{a}**1b** (0.04M) in acetone irradiated (300nm) for 60min. ^{b}Value for quenchable reaction, determined from plateau value (2.0) of Φ_o/Φ (-K). ^{c}**1e**(0.046M) in acetone irradiated (300nm: 55% conversion) after five freeze-thaw cycles.

The Stern-Volmer expression for loss of starting material or formation of product in a situation in which both sensitizer and substrate triplets may be quenched, is the quadratic equation 1.

$$\Phi_o/\Phi = (1 + k_q^K.\tau.[Q])(1 + k_q^S.1/\textstyle\sum k_{-S}.[Q]) \quad \text{------}1.$$

where k_q^K and k_q^S are the rate constants for quenching of enone and sensitizer triplets respectively. Since both piperylene (E_T 243.7 kJM^{-1}) and 1,3-cyclohexadiene (E_T 219 kJM^{-1})[10] have triplet energies much lower than either acetone (E_T 330.2 kJM^{-1}) or the enones under study

$(E_T$ 301-309 kJM$^{-1})^{cf.5d.}$ it was assumed that these rate constants could be taken as equal to k_{Diff} $(3.2\times10^{10}\ M^{-1}s^{-1})^{10,11}$. $\sum k_{-S}$ is the sum of the rate constants for those processes by which acetone triplets are destroyed, and may be regarded as the reciprocal of the lifetime of this species in the reaction medium. Differentiation of equation 1. reveals that the tangent to the curved Stern-Volmer plot at $[Q]=0$ should be equal to $k_{Diff.}(\tau + 1/\sum k_{-S})$. For the cases of **1b** and **1c** (see **Figure 2**) this quantity had the values 185 ± 50 and 330 ± 30 respectively. On the assumption that triplet quenching is diffusion-controlled these figures lead to combined lifetimes $(\tau + 1/\sum k_{-S})$ of 5.7 ± 1.5 ns for **1b** and 10 ± 1 ns for **1c**. Analysis of the data for **1c** (**Table V**) using a non-linear least squares regression program[12] gave essentially identical coefficients (230 and 235) for the quadratic expression 1. This led to values for τ and $1/\sum k_{-S}$ of 6.9 and 7.1 ± 0.7 ns. These values are in fair agreement with the result obtained by the simple construction of a tangent at the origin.



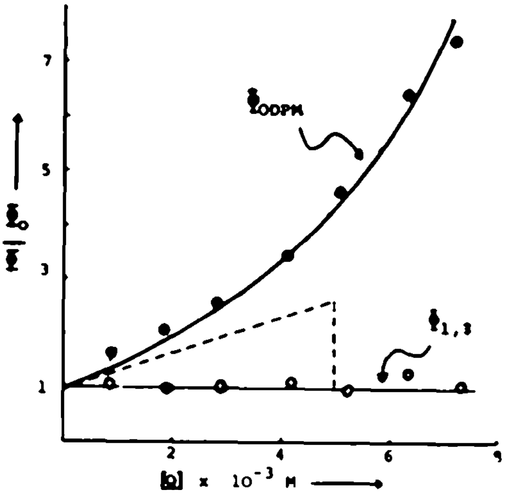


Figure 1: Irradiation of **1b**(0.065M): composition as function of time: o--**1b**, ●--**4b**, □--**5**, Δ--**9**, ▲--**9**(0.017M)

Figure 2: 1,3-Cyclohexadiene quenching of of the acetone-sensitized irradiation of **1c** (0.044M).

C. Triplet Sensitization Via Tetramethyldioxetane Thermolysis. It is well established[13] that the thermolysis of tetramethyldioxetane (TMD) results in the formation of a high yield of acetone triplets and a very small yield of acetone singlets. Experiments were performed in which degassed solutions of up to 0.75M TMD in benzene containing ~0.3M enone (**1a**,**1b** and **2**) were heated to 75°C and the products analysed both by GLC and by solution ir. In all three cases the yield of [1,3]-acyl shift product was much less than in photosensitized reactions carried out to the same conversion (ODPM yield)[6a]. In the case of **1a** the cyclobutanone carbonyl vibration could not be detected, in the case of **1b** it was barely detectable and in the case of **2** it was less than 20% of the value from the photochemical experiment.

DISCUSSION

The series of βγ-enones (**1a**-**c**,**2**), while superficially exhibiting the familiar dichotomy[1] between direct ([1,3]-acyl shift) and sensitized (ODPM) irradiation, have on closer examination, characteristic reactivities which add to our understanding of these reactions.

A. Direct Irradiation. The question of whether the [1,3]-acyl shift involves a concerted $({}_{\pi}2_s + {}_{\sigma}2_s)$ sigmatropic rearrangement or α-cleavage followed by radical recombination, has been debated since the first observation of this reaction[15]. There are to hand many examples of direct irradiation leading to characteristic radical-pair reactions: radical-recombination, disproportionation, decarbonylation etc.[16]. It has not always been clear however that the α-cleavage lay on the pathway to the [1,3]-acyl shift. More recently it has been shown unequivocably[17] that this reaction may follow either a singlet or triplet radical-pair pathway in certain cases. None of these results of course preclude the concerted pathway as a competing, or dominant process in some cases*. In particular the [1,3]-acyl shift observed on direct irradiation of **1a** has been claimed as an example of such a process[3]. This conclusion was based upon the observations that the reaction was not reversible, irradiation of **4a** yielding only cyclohexadie : and ketene, and that ketene did not appear to be a primary photoproduct. Houk[1c.] has pointed out that the results are equally compatible with α-cleavage being the primary photoreaction of both **1a** and **4a**, the resulting diradical reacting rapidly to give **4a** and only slowly to give ketene, recyclisation to **1a** being uncompetitive.

1b behaved in a very similar fashion, but the data of *Table II*, in spite of some scatter at short reaction times, confirmed that in this case fragmentation, presumably via α-cleavage, is competitive with [1,3]-acyl shift. This result carries no implications about the multiplicity of the intermediate diradical, or of the excited state from which it derives. The greater importance of fragmentation in the photochemistry of **1b** may reveal more facile α-cleavage. Alternatively it may merely indicate a 'looser' geometry for the diradical[19]. Either trend is in keeping with the known stabilizing effect of the methoxyl group on radical centres[20].

The formation of ODPM products on direct irradiation of **1a**,**1c** and **2** is particularly intriguing. The ODPM reaction on direct irradiation has rarely been reported, intersystem crossing to $T_1(\pi-\pi^*)$ being uncompetitive with processes leading to [1,3]-acyl shift[1,2]. Exceptions usually involve compounds in which the two chromophores are poorly aligned for interaction[21] or are not rigidly so aligned[cf.22]. In such cases the ODPM product is efficiently and selectively quenched by triplet quenchers. The idea that the reactions under discussion might also occur via intersystem crossing to T_1 was discounted by the observation that no differential quenching of the ODPM product by 1,3-cyclohexadiene was observed (see *Table I*). In contrast the production of the same compound by sensitized irradiation was efficiently quenched by concentrations of 1,3-cyclohexadiene one or even two orders of magnitude less.

These results would appear to represent the first examples of ODPM rearrangements originating from some excited state of a $\beta\gamma$*-enone (presumably* $\pi-\pi^*$*) other than* T_1. Further studies on the mechanism of this interesting and hitherto unsuspected photoreaction are described in the accompanying paper[23].

B. Sensitized Irradiation. The detailed mechanism of the photosensitized conversion of **5b** to **9** has not been studied by us, but may reasonably be supposed to arise by α-cleavage of the cyclopropane ring followed by the formal loss of the methyl group** and abstraction of a hydrogen atom (*Scheme I*). The cleavage reactions of cyclopropyl ketones are well-known[24] but do not normally appear to intervene in ODPM reactions. The stabilizing effect of the methoxyl group[20] on one of the radical centres of the proposed intermediate (**8**) may be considered adequate to explain the unusual behaviour of **5b**.

The T_1 lifetime of 7 ± 0.7 ns estimated for **1c** (*Table IV* and *Figure 2*) is in good agreement with the values of 4 ns obtained by a competitive quenching experiment[25a.] for bicyclo[4,4,0]dec-1(6)-en-3-one, and 6 ns obtained by a combined sensitization-quenching experiment[25b.] for 3-chlorobicyclo[3,2,1]oct-2-en-7-one. The construction of a tangent at the origin of the curved Stern-Volmer plot gives an upper limit for T_1 lifetimes, and may be thought more convenient, if less accurate than the Cristol method[26], especially in cases where relatively

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*A vapour-phase study of the photochemistry of **11** revealed that a part of the [1,3]-acyl shift arose via a process behaving towards quenchers as expected of a concerted process[18].

**It has been established that the methyl group is lost as a methyl radical by the observation of ethane among the products (K.Schaffner, *Personal communication*).

little substrate is available.

The values of $1/\sum k_{-S}$ for **1b** and **1e** (~7 ns) deserve further comment. $\sum k_{-S}$ would be expected to include the rate constant for intersystem crossing to ground-state acetone (k_{TS}), ($10^6 s^{-1}$)[10], and that for triplet energy transfer to the enone ($k_{ET}.[E]$). k_{ET} has been estimated by several groups[22,27] to be of the order of $1x10^7 M^{-1} s^{-1}$. At the concentration of enone (**1e**) used, k_{-S} should then have a value of $1.46x10^{-6}$ s^{-1} and $1/\sum k_{-S}$ a value of ~700 ns! This very large discrepancy between prediction and observation requires that an additional process for destruction of acetone triplets with a rate constant k_A ~10^8 s^{-1} operates in these systems, which are distinguished by the fact that virtually all the incident light is absorbed within the first 0.1-0.2 mm of neat acetone (15M) solutions. This will lead to a high concentration of acetone triplets in this region, compared with that produced in dilute solution of acetone. This in turn may lead to the possibility of triplet-triplet annihilation (equation 2)

$$Ac_T + Ac_T \text{ --- } \xrightarrow{k_{TT}} Ac_o + Ac_S \text{ ------ } 2.$$

The rate constant for this process (k_{TT}) usually approaches k_{Diff} and for benzophenone in Freon is $2x10^{10} M^{-1} s^{-1}$ [28]. For k_A (= $k_{TT}.[Ac_T]$) to reach the required value of $1.4x10^8 s^{-1}$ the concentration of acetone triplets in the narrow, absorbing region of solution would need to reach $3.4x10^{-3}$M. This does not seem an unattainable value, given the light intensities used (~$3x10^{17}$ photons s^{-1}).

Each of the four enones studied yielded ODPM products (**5a**, **5b** + **9**, **5c** and **7**) on irradiation in acetone, or in presence of acetophenone with quantum yields which fall within the expected range (Table IV)[1c]. The significantly lower quantum yield for the acetophenone vs. the acetone-sensitized reaction of **1b** suggests a value for E_T of ~310 kJM^{-1}, in accord with other estimates[5d.,27b.,36]. In all four cases, the [1,3]-acyl shift product was also formed, and its origin forms the subject matter of the remaining Discussion.

The early view of the [1,3]-acyl shift as originating from the $S_1(n-\pi^*)$ state of βγ-enones has been considerably modified in recent years[2]. As early as 1972, reports of sensitized [1,3]-acyl shifts began to appear[5d.,6a.,29], suggesting a triplet state origin for the reaction, although caveats about such interpretations were raised[1a.,6a.]. Important contributions by Schaffner[17,22] and Schuster[27b.] have firmly established that in certain cases the higher triplet state [$T_2(n-\pi^*)$] can be involved in the [1,3]-acyl shift either on direct irradiation by intersystem crossing, or on sensitization by high energy sensitizers. While the early reports of sensitized [1,3]-acyl shifts did not specify the triplet state involved, more recent papers[25b.,30] have stressed population of T_2 as the mechanism of these reactions. Support for this proposal is found in the lower efficiency of the process when acetophenone (E_T 310) rather than acetone (E_T 327kJM^{-1})[10] is used as the sensitizer (see Table IV).

It seemed to us that three mechanisms might in principle contribute to the sensitized [1,3]-acyl shifts: a). direct absorption of light by the substrate, b). singlet energy transfer from the sensitizer (in the case of acetone only in view of the very short lifetime of the acetophenone excited singlet state[10], and c). population of T_2 ($n-\pi^*$). Direct absorption of light by the substrate was considered and rejected by Engel[5d.] for the acetophenone-sensitized reaction of norbornenone, on the grounds that the enone did not absorb at 366 nm, the exciting wavelength used. Givens[25b.] on the other hand acknowledged that in the acetophenone-sensitized reaction of 3-bromobicyclo[3,2,1]oct-2-en-7-one (~0.01M) some light (~1.7%) was absorbed by the substrate, and was sufficient to account for the observed [1,3]-acyl shift in that case. In the cases of **1b** and **2** in our hands, the simple expedient of using soda-glass in place of pyrex vessels for the acetophenone-sensitized reactions revealed a selective reduction in the yield of the [1,3]-acyl shift product. Since soda-glass cuts out more light of wavelength < 320 nm[10] the clear inference is that a part at least of these reactions must be attributed to direct light absorption by the substrate. In acetone solution of course, direct absorption of light by the enone is always a contingency, and necessarily accounts for some part of the observed quantum yield of [1,3]-acyl shift product. Dauben[1a.] gave early warning of this impediment to the unambiguous assignment of triplet [1,3]-acyl shifts, and we have made the same caveat[6a.]. Ipaktschi[31], in a particularly clear-cut example showed that the acetone-sensitized [1,3]-acyl shift of **14** was concentration dependent*

The possibility that the $S_1(n-\pi^*)$ state of $\beta\gamma$-enones might be populated by singlet energy transfer (SET) from acetone has been raised on a number of occasions, but usually dismissed[5d.,25b.]. The question was directly and quantitatively addressed for the first time by Schuster[27b.] who studied the fluorescence quenching of acetone by the $\beta\gamma$-enone **12**. He was able to put a maximum value of $7\times10^9 M^{-1}s^{-1}$ on k_{SET}, and reached the conclusion that SET could account for no more than 15% of the observed value of $\Phi_{1,3}$ in the acetone sensitized irradiation of **12**.

A consideration of the quantum yields listed in Tables I and III, together with the results of sensitization via TMD thermolysis and the percentage of incident light absorbed by the substrate (Table V: estimated from the relative extinction coefficients of acetone and substrate) makes possible an assessment of the relative importance of the three mechanisms in the cases under discussion.

Table V. Direct Absorption of Incident Light During Acetone-Sensitized Reactions.

Enone(M)	ε(300nm)	% incident light absorbed[a]	$\Phi_{1,3}$(predicted)	$\Phi_{1,3}$(observed)
1a (0.098)	107	14.25	0.087	0.08
1b (0.065)	102	10.35	0.052	0.07[b] (0.094)[c]
1c (0.044)	122	7.36	0.049	0.045
2 (0.036)[d]	260	12.2	0.037	0.18
2 (0.099)[e]	260	27.0	0.081	0.16

[a] ε(acetone) = 4.5. [b] 55% conversion. [c] Calculated from data of Tables I. and IV. [d] Ref. 5d. [e] This study.

1a and **1c** are most simply dealt with. The data of Tables I,III and V suggest that direct absorption of light can account for all the [1,3]-acyl shift observed. This is strongly supported by the results of TMD thermolysis in presence of **1a**, which led to no detectable [1,3]-shift product. We conclude that in these cases photosensitization by acetone does not involve SET, and does not lead to significant sensitized population of the T_2 state**.

The analysis of the sensitized reactions of **1b** and **2** is more complex, since direct absorption of light can only account for part of the observed value of $\Phi_{1,3}$ (**1b**: 55-74%: **2**: 25-50%). TMD thermolysis experiments suggest that population of $T_2(n-\pi^*)$ is very unimportant (< 10%) in the case of **1b** but may account for ~20% of the value of $_{1,3}$ in the case of **2**. If the assumption is made that SET is responsible for the remaining yield of [1,3]-acyl shift in each case then, using the rate constant $(4\times10^8 s^{-1})$[10] for intersystem crossing for acetone, rate constants for SET for **1b** and **2** may be estimated to be $2.66-5.66\times10^8 M^{-1}s^{-1}$ and $0.74-6.5\times10^9 M^{-1}s^{-1}$ respectively. These fall within the upper limit for such a process estimated by Schuster[27b.].

Our analysis may be summarised as follows. 1). Enones **1a** and **1c** give no sensitized [1,3]-acyl shift products. The T_2 state of these ketones is not populated on acetone sensitization. 2). Both **1b** and **2** show behaviour which appears to require that SET be involved. They are the first examples of such behaviour, although direct evidence is lacking, and the estimated values of k_{SET} make it unlikely that such evidence will be available from simple acetone fluorescence-quenching experiments. 3). The T_2 state of **2** is populated on acetone-sensitization, although at the concentrations used only 20% of the observed yield of

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*The establishment of direct absorption of light by the substrate does not of course rule out $T_2(n-\pi^*)$, populated by intersystem crossing, as being partly or even solely responsible for the observed [1,3]-acyl shift.

The alternative possibility, that the T_2 states of these ketones yield no [1,3]-acyl shift product is partly discounted by the observation that thermal generation of **1c in this state leads to both ODPM and [1,3]-acyl shift products[23,32].

[1,3]-acyl shift product can be accounted for in this way[cf.5d.]. The evidence in the case of **1b** is more equivocal, but it seems likely that this process contributes slightly to the observed photochemistry.

The greater importance of SET in the photochemistry of **1b** and **2** may be rationalised in terms of their lower singlet energies (**1b** and **2**: E_S 359.5 kJM^{-1}: **1a** and **1c**: E_S 367.8 kJM^{-1}) as estimated from their absorption spectra. Assuming that the singlet-triplet (n-π*) splitting for this series of enones is similar, then the same rationale may be applied to the greater importance of T_2 in the sensitized photochemistry of **1b** and **2**. It may be relevant that in one other case (**12**) in which the T_2 origin of the [1,3]-acyl shift has been unambiguously established[27b.], the enone also has a low singlet energy (E_S = 359.5 kJM^{-1}).

The apparent delay in the buildup of ODPM products during the acetone-sensitized reactions of **1b** and **2** (*Figure 1* and ref. 5d.) may now be explained very simply. SET and absorption of light by the substrate, both of which are concentration dependent, will be more important in the early stages of the reaction. At higher conversions, triplet energy transfer, leading to population of the enone T_1(π-π*) state becomes dominant, resulting in a more rapid buildup of the derived ODPM products. At low initial concentrations of **1b** the effect, as expected on this analysis, becomes undetectable.

Finally, it seems worthwhile repeating our earlier warning[6a.] that in the sensitized photochemistry of βγ-unsaturated ketones, the diagnosis of triplet [1,3]-acyl shifts requires great caution, especially when the quantum yield for the process on direct irradiation is high. Absorption of light by the substrate is important in acetone, and may be so in acetophenone-sensitized reactions. Further, SET cannot be ignored, and the value of E_S seems important in this context.

EXPERIMENTAL SECTION

Instrumentation: Melting points were determined on a hot-stage, or in capillary, and are uncorrected. GLC was performed on a Pye Model 204 using 1/8in. x 4', and 1/8in. x 9' stainless steel columns. Preparative GLC was performed on the same instrument using a 1/4in. x 16' glass column, or on an F and M Prepmaster Model 75 using 3/4in. x 8' stainless steel columns. Spectra were obtained on the following instruments: nmr: Varian Model A60-A, Jeol Model FX100: ir: Perkin Elmer Models 125 and 225: uv: Unicam Model SP800-A: MS: Varian Model MAT CH-7. Irradiations were performed in a Rayonet reactor fitted with a merry-go-round sample holder and RPR 253.7, 300, and 350 nm lamps. Sample tubes were of quartz, pyrex or soda-glass.

Materials: All solvents were of Analar grade and were dried by standard procedures and stored over molecular sieves. The ketones (**1a–c** and **2**) were prepared by published procedures[4,33], and purified by distillation, preparative GLC and column chromatography. Nitrogen ('white spot') was freed from oxygen by bubbling through chromous chloride solution, and dried by passage through concentrated sulphuric acid and over KOH pellets.

Direct Irradiation of 1b 1). **1b** (0.3g) in ether (15 ml) was flushed with nitrogen for 15 minutes and irradiated (300 nm) in a quartz tube. GLC analysis after 2 minutes revealed a new peak with relative retention time (RRT) of 1.2 (relative to starting material), and more volatile components of RRT 0.09, 0.11 and 0.14. The longer retained peak grew to a maximum and then began to decay with time. Removal of solvent followed by preparative HPLC using chloroform:hexane (3:2) yielded three fractions. *Fraction 1* contained a mixture of 2,3-dihydroanisole, 2,5-dihydroanisole and anisole, identified by GLC, ir and nmr comparison with authentic samples. *Fraction 2* contained unreacted starting material and *fraction 3* contained a low yield of a compound identified as *3-methoxybicyclo[4.2.0]oct-2-en-8-one:* (**4b**). 2). **1b** (0.16g) in benzene (10ml) was flushed with nitrogen (15 min.) and irradiated (253.7 nm) for two hours in a quartz tube. Removal of solvent gave a product (0.055g) containing (by GLC) 95% of **4b** (RRT 1.2): uv, 290 nm: ir (neat), 2980,2930,2850,2830,1775 (C=O),1653 (C=C),1440,1370,1270,1165,1055,790,760,680 cm^{-1}: nmr, (CCl_4) δ 1.6-2.4 (5H: m), 2.6-3.1 (2H: ABXY, J_{AB} 6Hz), 3.53 (3H: s, OCH_3), 3.7 (1H: m) and 4.55 (1H: d, J=6Hz, vinyl proton). The *semicarbazone* (*ex* ethanol) had mp 205°: MS: 209 ($C_{10}H_{15}N_3O_2$, M^+).

To **4b** (0.1g) in 1,2-dimethoxyethane (DME: 10ml) was added 50% aqueous acetic acid (5ml) and the mixture stirred for 8 hours, poured into $NaHCO_3$ solution and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and evaporated. Preparative GLC gave *bicyclo[4.2.0]octan-3,8-dione* as a colourless oil: uv (MeOH) 295 nm(ε 30): ir (CCl_4) 1785 (cyclobutanone),1722 (C=O), 1450,1390,1360,1315,1120,1110 cm^{-1}: nmr (CCl_4), δ 1.9-3.7 (m's): MS: 138 ($C_8H_{10}O_2$, M^+), 110 (M^+-CO), 95 (110^+-CH_2).

Direct Irradiation of 1c **1c** (0.6g) in benzene (60ml) was placed in four phototubes, flushed with nitrogen, sealed and irradiated in a merry-go-round apparatus for 2 hours. GLC analysis of the product showed two new peaks (RRT 0.88 and 1.68) in the ratio of about 10:1. These were separated in >98% purity by preparative GLC. The larger fraction was identified as *1-methoxybicyclo[4.2.0]oct-4-en-7-one:* (**4c**): ir (neat) 3040,2930,2830,1780 (C=O),1640 (C=C),1440,1388,1347,1330,1250,1222,1110,1062,1042,1030,990,925,890,870,852,745,722 and 680 cm^{-1}:

nmr, δ 1.07-3.07 (7H: m), 3.31 (3H: s, OC$\underline{H}_3$), 3.59 (1H: d, J=6Hz), 5.51-6.11 (2H: m, vinyl protons). The minor product was identified as *1-methoxytricyclo[3.3.0.$0^{4,6}$]octan-3-one*, (5c), identical by GLC, uv, ir and nmr with the main product of sensitized irradiation of 1c.

Acetone-Sensitized Irradiation of 1b 1b (0.15g) in acetone (15ml) was flushed with nitrogen (15 min.) and irradiated (300 nm). After 5 min., new peaks with RRT 0.14, 1.1, and 1.2 were observed. After 30 min. a further peak (RRT 4.58) appeared. This continued to grow, and after 20 hr. was the dominant feature. Preparative GLC gave *bicyclo[3.3.0]octan-2,7-dione*, (9) as a white crystalline solid: mp 50-52°: ir (CCl_4) 1740 (C=O), 1400, 1360, 1170, 1150, 1120, 1090, 1070 cm^{-1}: nmr, δ 1.0-2.5 (complex m.): MS, 138 ($C_8H_{10}O_2$, M^+), 110, 96. A *semicarbazone* was prepared, mp 240°: MS 195 ($C_9H_{13}N_3O_2$, M^+). (*Found*: N, 21.40. *Calculated for* $C_9H_{13}N_3O_2$: N, 21.54%).

After 5 hr. irradiation the peak of RRT 1.1 was at its maximum. The products of several such irradiations were combined, solvents removed and subjected to preparative GLC. A low yield of the product was obtained in > 98% purity, as judged by GLC, and identified as *2-methoxytricyclo[3.3.0.$0^{2,8}$]octan-7-one*, (5b): uv (EtOH) 270 nm (ε 180), ir (CCl_4) 2940, 2860, 2820, 1745 (C=O), 1400, 1225, 1160, 1130, 1090, 1025, 695 cm^{-1}: nmr (CCl_4: 100MHz), δ 2.0 (2H: m), 3.62 (3H: s, OC$\underline{H}_3$): MS 152 ($C_9H_{12}O_2$, M^+), 137 (M^+- CH_3).

Irradiation of **5b** in acetone gave the diketone (9) as the only detectable product by GLC. This was also the only product formed on treatment of 5c in aqueous DME with toluene-p-sulphonic acid.

Acetone Sensitized Irradiation of 1c: 1c (0.606g) in acetone (60ml) was devided between 4 phototubes and irradiated as described. After 1 hr. GLC analysis showed a major new peak (RRT 1.68), and a minor peak (RRT 0.88). Removal of solvent from the aliquot and ir (CCl_4) analysis showed carbonyl peaks at 1720 (s) and 1780 (w) cm^{-1}. On the basis of GLC retention time and ir, the minor peak was identified as **4c**. After further irradiation for 6 hr., GLC analysis revealed that the peak of RRT 1.68 was the major component. Preparative GLC gave *1-methoxytricyclo[3.3.0.$0^{4,6}$]octan-3-one*, (5c) in 98% purity, as a colourless oil: uv (MeOH) 264 nm (ε 170): ir (neat) 2950, 2880, 2830, 1720 (C=O), 1325, 1310, 1225, 1140, 1115, 1090, 1005, 980, 930, 920, 882, 862, 810 cm^{-1}: nmr (CCl_4), δ 1.6-2.3 (7H: m), 2.5 (2H: broad s), 3.37 (3H: s, OC$\underline{H}_3$).

Quantum Yield Measurements. All measurements were performed in the cavity of a Rayonet Photochemical Reactor, using a merry-go-round attachment. All reactions were performed in quartz (300 nm) or pyrex (350 nm) phototubes, and were degassed before irradiation either by flushing with oxygen-free nitrogen, or by several freeze-thaw cycles on a vacuum-line. Light intensities were measured both before and after a series of determinations, using ferrioxalate [14,34] or benzophenone[10] actinometry. Chemical yields of products and conversions of starting materials were determined by GLC analysis using added acetophenone (1b), triglyme (1c) or diglyme (1a and 2) as internal standard. Relative response ratios of βγ-enones used were determined using a calibration curve derived from analysis of known mixtures of enone and standard. Integration was by triangulation or by use of a Varian Aerograph Model 480 Integrator. In the case of partially resolved peaks (e.g. **1b**, **4b** and **5b**) a DuPont Model 310 Curve Resolver was used. A minimum of three injections, and three phototubes were used in each determination. The estimated error is 10%. In the cases of **1a** and **2**, in which the starting material and [1,3]-acyl shift product were unresolved on GLC, additional analysis was performed by solution ir (CCl_4), using a Perkin Elmer Model 225 Spectrophotometer, and acetophenone as an internal standard.

Quenching Experiments: Quantum yields were determined as described above. Each tube contained an accurately weighed quantity of the appropriate quencher. The phototubes were degassed either by flushing with nitrogen, or by several freeze-thaw cycles before irradiation. In each determination, one tube without quencher was used as a standard.

TMD Initiated Reactions TMD[35] was prepared and stored at -20°C in small quantities (~50-100mg). Solutions of TMD (~0.75M) and the appropriate enone (~0.4M) in benzene were degassed with oxygen-free nitrogen, sealed and heated to 75° for 2 hr. The solvents were removed and ir (CCl_4), and GLC analysis performed.

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REFERENCES

1. a). Dauben, W.G.: Lodder, G.: Ipaktschi, J., *Top. Curr. Chem.*, 54, 73 (1975).
b). Hixson, S.S.: Mariano, P.S.: Zimmerman, H.E., *Chem. Rev.*, 73, 531 (1973). c) Houk, K.N., *ibid.*, 76, 1 (1976).
2. Schuster, D.I., *'Rearrangements in Ground and Excited States'*, pp.232-279, ed. P. de Mayo, Academic Press, N.Y., (1980).
3. Givens, R.S.: Oettle, W.F.: Coffin, R.L.: Carlson, R.G., *J. Amer. Chem. Soc.*, 93, 3957, 3963 (1971).
4. a). Evans, D.A.: Scott, W.: Truesdale, L., *Tetrahedron Lett.*, 121 (1972). b). Alfaro, I.: Ashton, W.: Rabone, K.L.: Rogers, N.A.J., *Tetrahedron*, 30, 559 (1974).
5. a). Schuster, D.I.: Axelrod, M.: Auerbach, J., *Tetrahedron Lett.*, 1911 (1963). b). Scheiss, P.: Funfschilling, P., *ibid*, 5191 (1972). c). Bays, D.E.: Cookson, R.C., *J. Chem. Soc. (B)*, 226, (1967). d). Scheznayder, M.A.: Engel, P.S., *Tetrahedron Lett.*, 1153 (1975).
6. a). Parker, S.D.: Rogers, N.A.J., *ibid*, 4389 (1976). b). Eckersley, T.J.: Parker, S.D.: Rogers, N.A.J., *ibid*, 4393.
7. Parker, S.D., *Ph.D. Thesis*, University of Lancaster, (1976).
8. Huckerby, T.N.: Rogers, N.A.J.: Sattar, A., *Tetrahedron Lett.*, 1113 (1967).
9. Demuth, M.: Schaffner, K., *Angew. Chem. (Int. Ed.)*, 21, 820 (1982).
10. Murov, S.L., *'Handbook of Photochemistry'*, pp. 7, 55, 107, 125, Marcel-Dekker, NY, (1973).
11. Turro, N.J., *'Modern Molecular Photochemistry'*, p.334, Benjamin/Cummings, (1978).
12. Beynon, R.J., *'PATTERNSEARCH'*, University of Liverpool, (1981).

13. Turro,N.J.: Lechtken,P.: Schore,N.E.: Schuster,G.: Steinmetzer,H.-C.: Yekta,A., *Acc.Chem.Res.*, **7**, 97 (1974).
14. Hatchard,C.G.: Parker,C.A.,*Proc.Roy.Soc.London,Ser.A*, **235**, 518 (1956).
15. Buchi,G.: Burgess,E.M., *J.Amer.Chem.Soc.*, **82**, 4333 (1960).
16. a). Baggiolini,E.: Schaffner,K., *Chem.Commun.*, 1103 (1969). b). Gonzenbach,H.-U.: Schaffner,K.:Blank,B.: Fisher,H., *Helv.Chim.Acta*, **56**, 1741 (1973). c). Paquette,L.A.: Eizember,R.F., *J.Amer.Chem.Soc.*, **89**, 6205 (1967): **90**, 5153 (1968). d). Paquette, L.A.: Henzel,R.P.: Eizember,R.F., *J.Org.Chem.*, **38**, 3257 (1973). e). Crandall,J.K.: Arrington,J.P.: Hein,J., *J.Amer.Chem.Soc.*, **89**, 6208 (1967). f). Sato,H.: Furutachi,N.: Nakanishi,K., *ibid*, **94**, 2150 (1972). g). Scharf,H-D.: Kusters,W., *Chem. Ber.*, **104**, 3016 (1971).
17. Henne,A.: Siew,N.P.Y.: Schaffner,K., *J.Amer.Chem.Soc.*, **101**, 3671 (1979): *Helv.Chim.Acta*, **62**, 1952 (1979).
18. Beimann,B.: Sadler,D.E.: Schaffner,K., *Unpublished Results*. A preliminary account of this study was given at the Annual Congress of the RSC, Lancaster, (1983). We are grateful to Professor Schaffner for communicating results prior to publication.
19. Michl,J., *Chemical Reactivity and Reaction Paths*, pp. 301-338, ed. Klopman,G., Wiley-Interscience, NY, (1974).
20. a). Cruickshank,F.R.: Benson,S.W., *J.Amer.Chem.Soc.*, **91**, 1289 (1969). b). Martin,R.H.: Laupe,F.W.: Taft,R.W., *ibid*, **88**, 1353 (1966).
21. Engel,P.S.: Schexnayder,M.A.: Ziffer,H.: Seeman,J.I.,*ibid.*, **96**, 924 (1974).
22. Mirbach,M.J.: Henne,A :Schaffner,K., *ibid.*, **100**, 7127 (1978). The 3-acetylcyclopentene series may be atypical. In those cases in which it has been observed, the ODPM product has not been selectively quenched. We are grateful to Professor Schaffner for this information.
23. Eckersley,T.J.: Rogers,N.A.J., This Journal, Accompanying Paper.
24. a). Dauben,W.G.: Welch,W.M., *Tetrahedron Lett.*, 4531 (1971). b). Witkop,B.: Kunieda,T., *J.Amer.Chem.Soc.*, **93**, 3478 (1971).
25. a). Engel,P.S.: Schexnayder,M.A.: Phillips,W.V., *Tetrahedron Lett.*, 1157 (1975). b). Givens,R.S.: Chae,W.K.: Matuszewski,B., *J.Amer.Chem.Soc.*, **104**, 2456 (1982).
26. Cristol,S.J.:Kaufman,R.L., *J.Photochem.*, **12**, 207 (1980).
27. a). Loufy,R.O.: Yip,R.W.: Dogra,S.K., *Tetrahedron Lett.*, 2843 (1977). b). Schuster,D.I.: Calcaterra,L.T., *J.Amer.Chem.Soc.*, **104**, 6397 (1982).
28. Ref. 11, p.343..
29. a). Murray,R.K.: Babiak,K.A., *Tetrahedron Lett.*, 319 (1974). b). Engel,P.S.: Schexnayder,M.A., *J.Amer.Chem.Soc.*, **94**, 2252 (1972): **97**, 145 (1975).
30. Schaffner,K., *Tetrahedron*, **32**, 641 (1976).
31. Ipaktschi,J., *Chem.Ber.*, **105**, 1840 (1972).
32. Eckersley,T.J.: Rogers,N.A.J., Presented in part as a Poster at the Annual Congress of the RSC, Lancaster, April, (1983).
33. a). Freeman,P.: Balls,D.: Brown,D.: Wildman,W.: Saunders,D., *J.Org.Chem.*, **16**, 381 (1951). b). Freeman,P.: Balls,D.: Brown,D., *ibid*, **33**, 2211 (1968). c). Alfaro,I.: Ashton,W.:,McManus,L.D.: Newstead,R.C.: Rabone,K.L.: Rogers,N.A.J.: Kernick,W., *Tetrahedron*, **26**, 201 (1970).
34. Calvert,J.G.: Pitts,J.N.Jr., *'Photochemistry'*, pp.783-786, Wiley, NY, (1966).
35. Kopecky,K.R.: Filby,J.E.: Mumford,C.: Lockwood,P.A.: Ding,J.Y., *Canad.J.Chem.* **53**, 1103 (1975).
36. Gonzenbach,H-U.:Tegmo-Larsson,I-M.:Grosclaude,J-P.:Schaffner,K., *Helv.Chim.Acta*, **60**, 1091 (1977).