Tetrahedron Vol. 40, No. 19, pp. 3759 to 3768, 1984
Printed in the U.S.A.

0040-4020/84 $3.00+.00
Pergamon Press Ltd.

PHOTOCHEMICAL STUDIES ON BICYCLIC $\beta\gamma$-UNSATURATED KETONES: II^1. OXADI-π-METHANE REARRANGEMENTS ORIGINATING FROM SOME STATE OTHER THAN T_1 (π-π^*).

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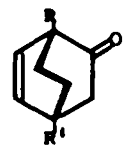
(*Received in UK* 22 *May* 1984)

Abstract-the unquenchable ODPM reaction observed on direct irradiation of three $\beta\gamma$-unsaturated ketones has been studied in solution and in the vapour-phase. The results suggest that the higher triplet state might be the origin of this reaction. Thermal generation of this excited state in one case supports the conclusion. The vapour-phase results further suggest the existence of both diradical and concerted pathways for the [1,3]-acyl shift from the excited singlet state, and the possibility of a similar pattern from the higher triplet state.

Early studies on the oxadi-π-methane (ODPM) rearrangement^2 (e.g. $1 \dashrightarrow 3$: $2 \dashrightarrow 4$) indicated that the reaction occured from the lowest excited triplet state (T_1, π-π^*). In earlier communications^{1,3} we have reported that the $\beta\gamma$-enone **1b** yields the ODPM product **3b** on direct irradiation as well as on sensitization by acetone or acetophenone. Similar behaviour was exhibited by **1a** and **2**. That different excited states were involved in the two modes of reaction was indicated by quenching experiments: no selective quenching was observed in the direct irradiations, while the sensitized ODPM reaction was efficiently quenched^1. There are very few indications in the literature^4 that the ODPM reaction might arise from any excited state other than T_1 (π-π^*), and this paper documents some of our investigations into the origin of this unusual photoreaction.



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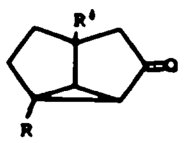

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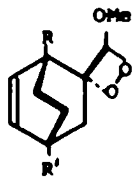
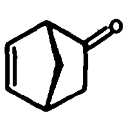


5.

a. R=R'=H
b. R=H, R'=OMe
c. R=OMe, R'=H



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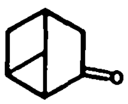

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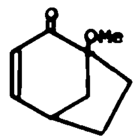


6.

RESULTS

A: Solution Photochemistry. The solution photochemistry of **1b** has been reported[1,3]. The published data on the photochemistries of **1a**[5] and **2**[6] give no indication of an ODPM rearrangement accompanying the [1,3]-acyl shift on direct irradiation. Very careful reinvestigation of these reactions revealed small but reproducible yields of ODPM products (**3a** and **4**). In both cases,these products remained unquenched in presence of quite high concentrations of 1,3-cycohexadiene (Table I). This is in marked contrast to the efficient quenching observed in the sensitized ODPM reactions.

Further evidence that the ODPM rearrangement was occuring from two distinct excited states of **1b** on acetone sensitization was obtained from quenching experiments with piperylene[3c]. At low quencher concentrations the expected curved Stern-Volmer plot was obtained [cf.1]. At high quencher concentration (0.1M) this curve showed signs of levelling off, implying that reaction was also arising from some more short-lived state.

Table I: Solution Photochemistry of **1a**, **1b** and **2** (300nm).

Enone	Quencher[a] (M)	Φ_{-K}	$\Phi_{1,3}$	Φ_{ODPM}	$\Phi_{1,3}/\Phi_{ODPM}$	Time (min.)
1a	0	0.58	0.39	0.017	2.3	30
1a	0.15	0.46	0.37	0.016	23(61)[b]	30
1b	0	0.5[c]	0.29[c]	0.025[c]	11.5	40
1b	0.19	0.39	0.24	0.022	11.0(6.9)[b]	40
2	0	0.71	0.29	0.004	73	37
2	0.14	0.54	0.22	0.009	22(101)[b]	37

[a] 1,3-Cyclohexadiene. [b] 254nm. [c] Values taken from plot of Φ against time[1] and used to determine light intensities in this series of experiments.

B: Attempted Thermal Generation of Triplet $T_2(n-\pi^*)$ States. 1,2-Dioxetanes, on thermal decomposition are well-known[7] to yield carbonyl compounds in the triplet excited state. In the case of tetramethyldioxetane the ratio of triplets to excited singlets of acetone produced is of the order of 100:1[8]. It seemed to us that the decomposition of dioxetanes such as **5** might be expected to yield the $T_2(n-\pi^*)$ states of the ketones **1**, since the excitation associated with the thermolysis should be concentrated on the carbonyl function. We were encouraged in this view by the publication by Schaffner[9] of results of the thermolysis of **7**. His data was interpreted in terms of the initial production of the $T_2(n-\pi^*)$ state, which yielded the [1,3]-acyl shift product **9** and (supposedly by prior internal conversion to $T_1(\pi-\pi^*)$) the ODPM product (**10**), (Scheme I).

Our first attempts along these lines were directed at **5e** because of the ready availability of enone **1c**[10]. Reaction with $MeOCH{=}PO_3$[11] gave the enol ethers **11** and **12** in fair yield, and in about equal quantities, as judged by GLC analysis. Attempted purification by distillation gave a single isomer, the nmr spectrum of which showed it to be **12** (Scheme II). Enone **1b** on similar treatment gave two products (**14** and **15**), in comparable yield, although here again the ratio appeared to change on distillation, separable in 98% purity by preparative GLC. Their structures were assigned on the basis of their nmr spectra (see Experimental section).

Attempted photooxidation[12] of the enol ethers **12**, **14**, and **15** proved disappointing. In all three cases photooxidation was efficient, as measured by the disappearence of the starting material, but only in the case of the Z-isomer **15** was there any indication of dioxetane formation, and even in that case it was very much the minor product. In all cases, hydroperoxide formation was the preferred mode of reaction (Scheme II). Thermolysis of the photooxidation mixtures led, in the cases of **12** and **14** to no recognisable products. In the case of **15** however small quantities of materials, identical by GLC to the [1,3]-acyl shift and ODPM products, were observed. The relative proportions of these products obtained on direct irradiation, on sensitized irradiation, and on thermolysis of the dioxetane (**18**) are listed in Table II.

Scheme I

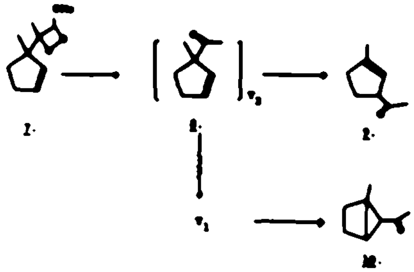
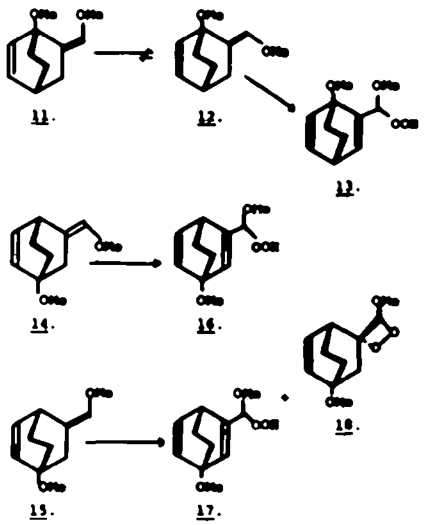


Table II: [1,3]-acyl shift and ODPM products of **1b** : dependence of relative importance on route of formation.

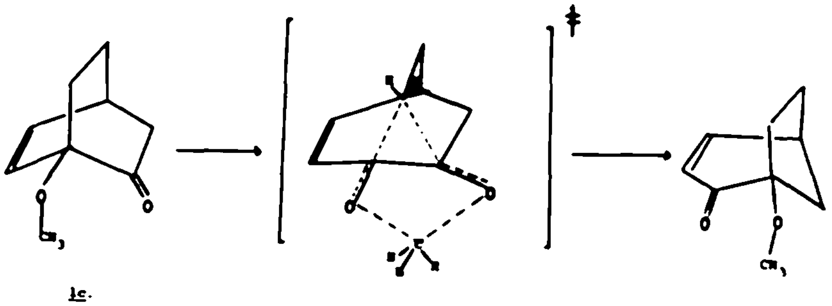
Conditions.	$\Phi_{1,3}/\Phi_{ODPM}$
Direct Irradiation.	11.0
Acetone Sensitization.	0.30
Thermolysis of **18**.	2.35

Scheme II



C. Flash Vacuum Thermolysis Experiments. It has been suggested[13] that a possible mechanism for some [1,3]-acyl shift reactions might involve excitation to $S_1(n\text{-}\pi^*)$ followed by return to the ground-state PE-surface on which rearrangement subsequently occurs. In the case in question, a thermal [1,3]-acyl shift had also been observed[14]. We explored this possibility in the cases of **1b** and **1e**. The ketone was allowed to distil under vacuum (mercury diffusion pump) through a tubular silica furnace (20cms.) heated to temperatures between 300 and 500°C. The distillate was collected in a liquid nitrogen trap. In neither case was any photoproduct observed, but enone **1e** gave a clean (~50% chemical yield) conversion to the conjugated enone **6**. This is also the product of the non-aqueous acid-catalysed rearrangement of **1e**[10]. Further work is needed to establish if this thermal process is a surface acid-catalysed reaction, or an unusual, but allowed ($_\pi2_a + {}_\sigma2_a + {}_\sigma2_s$) pericyclic reaction (Scheme III).

Scheme III



D: Vapour Phase Studies. Qualitative studies were performed on enones 1a, 1b and 2. The enones were introduced as vapour into a quartz reaction vessel evacuated to 10^{-4} torr. (see Experimental section), and irradiated (300 or 253.7 nm) in the cavity of a Rayonet photochemical reactor for varying periods of time. The products were then condensed, dissolved in solvent and analysed by GLC and solution ir. The results revealed that the importance of the [1,3]-acyl shift relative to the ODPM reaction was much reduced in the vapour-phase and that a wavelength effect existed, the ratio in question being lower at 253.7 than at 300 nm. There also appeared to be a minor wavelength effect in solution (Table I). No indication as to whether these changes reflected a decrease in $\Phi_{1,3}$ or an increase in Φ_{ODPM} (or both) could be obtained from these results.

Table III: Quantitative Vapour Phase Results.

Enone	Time (sec.)	Φ_{-K}	$\Phi_{1,3}$	Φ_{ODPM}	$\Phi_{1,3}/\Phi_{ODPM}$
1a	600	0.53	0.02	0.003	6.7
1b	300	-[a]	0.03	0.04	0.8
1b	900	0.56	0.11	0.023	4.8
1b	2580	0.27	0.01	0.005	2.0
2	900	0.35	0.05	0.005	10.0
2	900	-[a]	0.04	0.004	10.0

[a] Apparent values of Φ_{-K} were impossibly large (>1) in these experiments: see discussion.

Quantitative experiments were performed using 2-hexanone actinometry[15]. In view of the low volatility of the substrates, and the very low proportion of the incident light absorbed in these irradiations, calculations of quantum yields were based upon GLC analysis using an internal standard (diglyme, 1a and 2: triglyme, 1b), and the relative solution extinction coefficients of substrates and 2-hexanone. Experiments were also performed in presence of nitrogen and of xenon (15torr.). The results are listed in Table IV.

Table IV: Effect of Inert Gasses on Vapour Phase Photochemistry.

Enone	Time(sec.)	Φ_{-K}	$\Phi_{1,3}$	Φ_{ODPM}	$\Phi_{1,3}/\Phi_{ODPM}$
A. Nitrogen (15 torr.)					
1a	900	0.34	0.12	0.002	60
1b	300	-	0.06	0.022	2.7
2	600	0.62	0.06	0.002	30
B. Xenon (15 torr.)					
1a	900	0.56	0.16	0.003	53.3
1b	300	-	0.08	0.019	4.2
2	600	0.46	0.018	0.003	5.3

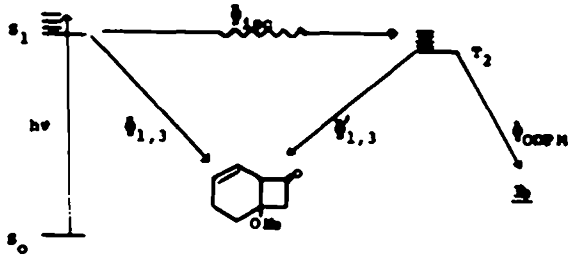
DISCUSSION

Solution Phase Experiments. Photolyses in solution showed quite clearly that in the case of the three βγ-unsaturated ketones 1a, 1b and 2, the ODPM rearrangement originates, rather inefficiently, from some state other than $T_1(\pi-\pi^*)$ as well as, efficiently, from that state on sensitization. No identification of the state responsible was possible from these experiments, although the quenching studies indicated that it was of short lifetime. The present state of knowledge of $\beta\gamma$-enone photochemistry[2,16] would point to $S_1(n-\pi^*)$ or $T_2(n-\pi^*)$, (or possibly both) as the origin of this unusual photoreaction.

Dioxetane Thermolysis. The formation and thermolysis of dioxetanes such as 18 turned out, in our hands to be very unpredictable and sensitive to structure. Our limited success in this area is open to more than one interpretation.

1). Thermolysis leads to formation of the $T_2(n-\pi^*)$ state, which then partitions between [1,3]-acyl shift and ODPM rearrangement. If the further assumption is made that internal conversion from $T_2(n-\pi^*)$ to $T_1(\pi-\pi^*)$ is uncompetitive with processes leading to reaction[cf.17], then the solution photochemistry of 1b can be represented by Scheme IV. Qualitatively similar schemes could presumably describe the photochemistries of 1a and 2.

Scheme IV



$\Phi_{1,3} = 0.37$
$\Phi_{isc} = 0.187$
$\Phi'_{1,3} = 0.7$
$\Phi_{ODPM} = 0.3$

2). Thermolysis leads to the T_2 state which then partitions between [1,3]-acyl shift and internal conversion to $T_1(\pi-\pi^*)$ which in turn yields the ODPM product. This scheme would rule out T_2 as an important contributor to the solution photochemistry of 1b, since in that case the ODPM product formed on direct irradiation is unquenchable. Clearly intermediate possibilities also exist and future experiments to clarify this issue must include the pyrolysis of dioxetanes such as 18 in presence of efficient triplet quenchers.

Finally, the assumption that the thermolysis of such dioxetanes must lead to the production of the $T_2(n-\pi^*)$ state may itself be suspect in the case of conformationally rigid systems such as 18. The (presumably) sterically preferred endo-photooxidation may well lead on thermolysis to interaction with the orbitals of the alkene moiety, and direct production of the $T_1(\pi-\pi^*)$ state. Here again, thermolysis experiments in presence of quenchers are indicated. Work is in hand designed to avoid the preparative difficulties encountered in this study, and to probe the involvement of $T_1(\pi-\pi^*)$ in the thermolyses.

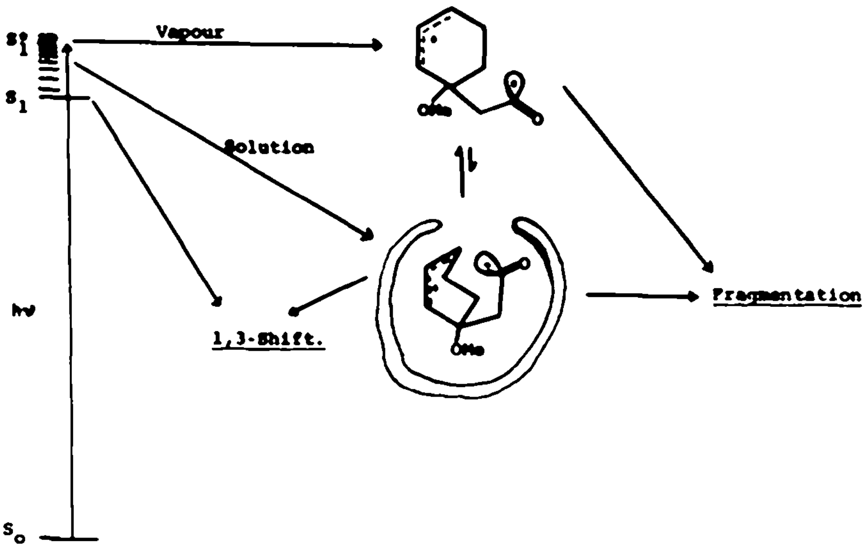
Vapour-Phase Experiments. Many vapour-phase studies on carbonyl compounds have been reported, and the subject has been reviewed[18]. To our knowledge, the only other vapour-phase study of a $\beta\gamma$-unsaturated ketone is that by Schaffner[19] on the 3-acetylcyclopentene (8), conducted in presence of a sufficient pressure of inert gas to ensure that the excited states involved were fully vibrationally relaxed before reaction. Our experiments were conducted in the first instance at low pressures (~0.1torr.) which approximate to 'isolated molecule' conditions, in the hope of seeing changes in reactivity which could be associated with vibrational excitation, and probed by collisional relaxation in presence of inert gases.

The results described here must be regarded as preliminary in nature, and inherently somewhat inaccurate. This is particularly true of the values of Φ_{-K}: those of $\Phi_{1,3}$ and Φ_{ODPM} carry greater confidence. In spite of these caveats, some clearly defined trends are revealed and tentative conclusions may be drawn which are sufficiently novel in the context of current theory[2,16] to merit discussion at this stage.

A. The data of Tables I and IV show that $\Phi_{1,3}$ is dramatically reduced compared with its value in solution, while Φ_{ODPM} is but little affected. At the same time, the efficiency of fragmentation processes are high in the vapour-phase, and the values of Φ_{-K} , while intrinsically unreliable, do not seem to be markedly lower than in solution. The effect of added nitrogen is to increase $\Phi_{1,3}$ but not to restore it to the solution value.

A simple interpretation of these observations could be that α-cleavage to a singlet diradical is very efficient from the higher vibrational levels of $S_1(n-\pi^*)$. In solution the radical centres, constrained within bonding distance by the solvent cage can lead relatively efficiently to [1,3]-acyl shift, or to fragmentation products. In the vapour-phase the excess energy of the vibrationally unrelaxed singlet state (S_1^*,n-π^*) should result in vibrational and rotational motions of the diradical, placing it in a conformation from which fragmentation is favoured (<u>Scheme V</u>). The effect of added nitrogen (15torr.) must be to bring about vibrational relaxation of the $S_1(n-\pi^*)$ state$^{cf.21,22a.}$. The enhanced value of $\Phi_{1,3}$ under these conditions is interesting, since even at the lowest vibrational level of S_1 (E_S = 359.5kJM^{-1})^1 the energy is much in excess of that required to bring about α-cleavage^{20}. The results would appear to indicate that from the lower levels of S_1, a <u>concerted</u> ($_{\sigma}2_s + _{\pi}2_s$) [1,3]-acyl shift occurs in each of the three cases studied.

<u>**Scheme V**</u>



These results are in general agreement with Shaffner's^9 and Schuster's^{17} observation of a diradical route to the [1,3]-acyl shift from $S_1(n-\pi^*)$ involving an activation barrier. Similar conclusions have been derived from the vapour-phase photochemistries of cyclobutanone, cyclopentanone and 7-norbornanone^{21,22}. The wavelength effect in the solution photochemistry of **1b**, irradiation at 254nm populating higher vibrational levels of S_1 than at 300nm is also in line with this analysis. The conclusion that a concerted route to the [1,3]-acyl shift product might be followed from the vibrationally relaxed S_1 state is supported by the study^{19} of the vapour-phase photochemistry of **8**. Addition of nitric oxide or oxygen led to substantial quenching of the [1,3]-acyl shift, but a residual reaction behaved as though concerted.

It should be noted that an alternative interpretation of these results is possible. It is known that for simple carbonyl compounds the rate of non-radiative decay of the $S_1(n-\pi^*)$ state is dramatically enhanced by excess vibrational energy. In more than one case the enhancement has been related to an increase in the rate of internal conversion (S_1^*--- ^{k}IC--→ S_o^*)^{23}. It may be that our results can be accounted for in terms of internal return to a 'hot' ground state (S_0^*) from which α-cleavage is efficient in the absence of collisional relaxation[*].

This analysis would predict that Φ_{-K} should decrease in presence of moderate pressures of nitrogen, through vibrational relaxation of the 'hot' ground state. Our present techniques are inadequate to test this hypothesis, but work is in hand which will allow more precise measurement of Φ_{-K}.

B. The effect of added xenon is particularly interesting (Table V). In the cases of **1a** and **1b** the effect is not markedly different from that of nitrogen, although the slight increase in $\Phi_{1,3}$ might be a real effect. In the case of **2**, no increase in $\Phi_{1,3}$ relative to the low pressure experiment was observed. In all three cases the effect on Φ_{ODPM} was too small to merit comment at this stage.

The ability of xenon, like other heavy atoms, to enhance intersystem crossing by spin-orbit coupling is widely known[24], although no such perturbation has been observed in the photochemistry of simple carbonyl compounds[25]. More recently, Schuster[17] has shown that the process $S_1 \xrightarrow{k_{isc}} T_2(n\text{-}\pi^*)$ is enhanced in solution by xenon. To our knowledge, no other study on the effect of xenon on the vapour-phase photochemistry of βγ-enones has been reported.

Our preliminary results must obviously be interpreted with considerable caution. Our basic assumption was that differences in the effects of nitrogen and xenon could be attributed to enhanced intersystem crossing to T_2 in the latter case. On this basis we must conclude that **2** in presence of moderate pressures of xenon undergoes efficient intersystem crossing to $T_2(n\text{-}\pi^*)$ from which the dominant reaction is α-cleavage leading to fragmentation products. The unchanged, or possibly slightly raised value of Φ_{ODPM} in this system would point to T_2 as the origin of the ODPM reaction.

The results from experiments with **1a** and **1b** were more ambiguous. If we reasonably assume that in these cases also, intersystem crossing to T_2 is enhanced by xenon, then these less strained ketones preferentially undergo a [1,3]-acyl shift from T_2, presumably via an unusual[27] tight diradicaloid pathway. In both cases, T_2 is also the origin of a rather inefficient ODPM reaction[**].

We have assumed in this discussion that in the vapour-phase, as in solution[1] the $T_1(\pi\text{-}\pi^*)$ state is not populated either by intersystem crossing from S_1 or by internal conversion from T_2. single experiment in which 1,3-cyclohexadiene (~15torr.) was introduced to the reaction vessel produced no selective quenching of the ODPM product.

C. Summary. 1). The βγ-enones **1a**, **1b** and **2** give rise to ODPM reactions on sensitization (from the $T_1(\pi\text{-}\pi^*)$ state) and also, on direct irradiation from the $T_2(n\text{-}\pi^*)$ state, (or less probably, from the $S_1(n\text{-}\pi^*)$ state). The quantum yield (Φ_{ODPM}) on direct irradiation is, in the cases of **1a** and **1b**, comparable with that observed in the only other unambiguous case of an ODPM reaction originating from some other state than $T_1(n\text{-}\pi^*)$[4]. It is tempting to think that this reaction may be of more general occurence. A possible example in the literature is the ODPM reaction ocurring on direct irradiation of 3-acetylcyclopentenes[9,26]. It is also tempting to speculate that this reaction may be an example of the illusive $({}_{\pi}2_a+{}_{\sigma}2_a)$ mechanism for the ODPM rearrangement, rather than the commonly observed diradical pathway[cf.2]. The stereochemistry observed in the case of E-1-cyano-3,3,5-trimethylhex-1-en-4-one[4] lends support to this speculation.

2). The [1,3]-acyl shift can arise in the case of **1b** (and possibly also the other enones studied) from both the S_1 and T_2 states in line with recent reports on other enones[9,16]. Elevated temperatures (254nm in solution: 'isolated molecule' conditions in the vapour-phase) appear to favour a singlet diradical pathway leading predominantly to [1,3]-acyl shift in solution,

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[*] The absence of [1,3]-acyl shift or ODPM reaction in the Flash Vacuum Thermolysis experiments does not conflict with this interpretation, since at the low pressures involves (~0.1torr.) fragmentation would be expected to predominate.

[**] The alternative interpretation, that $S_1 \dashrightarrow T_2$ is not perturbed by xenon seems unlikely, unless this process is already efficient in these enones. In either case this view would point to both S_1 and T_2 as the origin of the ODPM reactions.

and to fragmentation in the vapour.

3). There is evidence for a triplet diradical pathway in the vapour-phase photochemistry of 2. If perturbation by xenon is effective in all three cases then 1a and 1b react from T_2 in a manner expected for a concerted [1,3]-acyl shift.

4). While there is no evidence of photochemical acyl-shift products occuring from a 'hot' ground state in the vapour-phase, the possibility that this process contributes to solution [1,3]-acyl shifts and to vapour-phase fragmentation cannot be ruled out.

While these conclusions must be regarded as tentative at this stage, our results do suggest that the photochemistry of bicyclic βγ-enones may be considerably more complex than is currently accepted[2,16]. Further work is indicated and planned to test these conclusions. It is worth noting that the identification of excited states involved in the photochemistry of these bicyclic enones is hampered by the absence of detectable fluorescence in our hands.

EXPERIMENTAL

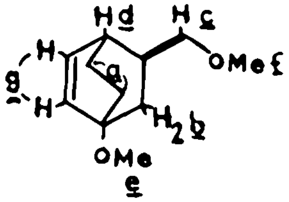
Instrumentation and materials are as described in the preceding paper.

E-1-Methoxy-2-methoxymethylenebicyclo[2.2.2]oct-5-ene (12). To methoxymethyltriphenyl phosphonium chloride (13.6g) suspended in sodium dried ether (500ml), cooled to -80° and under an atmosphere of dry nitrogen, was added butyl lithium (1.6M: 25ml) in hexane. After 5 min. stirring, the enone (1c: 2.0g) in ether (10ml) was added and the solution allowed to warm to room temperature and stirred for 24 hr. The solvent was removed and the residue suspended in pentane (100ml), filtered and the filtrate washed with pentane (2x50ml). Removal of the solvent gave the crude product (2.5g) as a yellow oil. GLC revealed four components: enone 1c (13.3%), Z-11 (37.5%): E-12 (39.8%) and an unidentified component (9.4%). The crude product was distilled twice using a Hickman still (1torr.) to give a colourless liquid (1.25g). GLC analysis showed this to be largely E-12 (78.7%), containing no detectable Z-isomer: also present were the parent enone (1c: 15.1%) and an unidentified, more volatile component (7.7%). Attempts at further purification by preparative GLC or column chromatography led to decomposition.

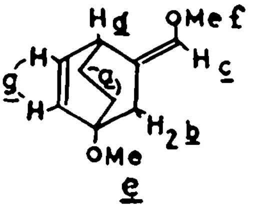
Spectral data (after removing signals associated with the enone 1c) were as follows: ir: 3060, 2870, 2840, 1680 (C=C), 1465, 1440, 1370, 1330, 1305, 1270, 1255, 1225, 1125, 950, 910, 855, 870, 750, 700 cm^{-1}. nmr: (CCl_4: 60MHz) δ 0.68-1.85 (4H: complex m), 1.9-2.21 (2H: doublet of doublets: J_{AX} 5Hz, J_{AY} 2Hz), 2.28-2.68(1H: m), 3.28(3H: s, bridgehead $OC\underline{H}_3$), 3.43 (3H: s, $OC\underline{H}_3$), 5.75-5.91(1H: t, J_{YA} 2Hz), 5.91-6.41 (2H: m). This material was used in photooxidation experiments without further purification.

E- and Z-1-Methoxy-5-methoxymethylenebicyclo[2.2.2]oct-2-ene (14 and 15). The procedure was exactly as in the previous experiment except that after warming to room temperature the mixture was stirred for only 1 hr. Methoxymethyltriphenylphosphonium chloride (9.04g), enone 1b (1.2g) and butyl lithium (1.6M in hexane: 12.36ml) gave 1.5g. of a crude product. GLC revealed the presence of five volatile components: unchanged enone (11.5%), 14 (17.0%), 15 (31.5%) and two unidentified components (25.6 and 14.6%). Distillation (twice) using a Hickman still (bp 68-88°) gave a colourless, viscous oil (0.7g). GLC analysis showed the same five components, 1b (11.1%), 14 (30.5%), 15 (34.2%), and unidentified components (15.8 and 8.4%). Ir (after removal of peaks associated with 1b) showed peaks at 3105, 2965, 2885, 1690 (C=C),1610, 1460, 1365, 1325, 1305, 1285, 1265, 1240, 1205, 1180, 1105, 1035, 1005, 985, 960, 925, 835, and 785 cm^{-1}.

Preparative GLC gave samples of 14 and 15 in greater than 98% purity as judged by GLC. They were identified by their nmr spectra, detailed below.



14. δ 1.14-1.89 (4H: complex m, H_a), 2.13-2.34 (2H: broad d, J_{bc} 2.5Hz, H_b), 2.56-2.89 (1H: complex m,H_d), 3.39 (3H: s, H_e), 3.53 (3H: s, H_f), 5.81-5.98(1H: t, J_{cb} 2.5Hz, H_c), 6.19-6.43 (2H: complex ,m, H_g).



15. δ 1.17 (4H: complex m, H_a), 2.19 (2H: broad s, H_b), 2.55-2.82 (1H: complex m, H_d), 3.37 (3H: s, H_e), 3.52 (3H: s, H_f), 5.73 (1H: broad s, H_c), 6.18-6.33 (2H: complex m, H_g).

Reactions of 12, 14, and 15 with singlet oxygen. The diene (50mg) in Freon 11 (20ml) was placed in the outer cavity of a double-walled vessel equipped with a magnetic stirrer, and optical windows. Polymer-bound Rose Bengal[28] (400mg) was added, and a stream of oxygen passed through the stirred solution via a capillary. The reaction mixture was cooled to -78° by means of acetone-Drikold in the inner vessel, and irradiated for one hour with a 1000 watt tungsten lamp. The solution was concentrated at low temperature, and the nmr spectrum measured. The important signals were: from 12, δ 5.25 (s): from 14, δ 5.00 (d, J=2Hz), and from 15, δ 5.02 (s) and 5.33 (s). After removal of the solvent, the product was dissolved in benzene (50ml) and heated to 80° for 20 min., evaporated and analysed by GLC. In the case of 15 the [1,3]-acyl shift and ODPM products were identified by adding authentic samples and repeating the analysis. The assignments were supported by nmr (several OMe signals, including weak signals at δ 3.37 (4b) and δ 3.31 cf.1, and solution ir analysis (presence of peak at $1780cm^{-1}$.

Vapour-Phase Photochemistry.

Equipment. The reaction vessel was a quartz flask (1.235 l) which could be attached to a vacuum line equipped with an oil diffusion pump capable of evacuating the system to 10^{-5}torr. Also attaced to the system was a reference flask (pyrex: 1.15 l) and sample flasks (10 to 100ml).

Procedure. The sample was thoroughly degassed, using five freeze-thaw cycles and then closed off from the rest of the system which was evacuated to $\sim10^{-5}$ torr. The sample flask was then opened to the reaction vessel and the sample flask and allowed to equilibrate at ambient temperature. Both flasks were then sealed from the system and removed. The sample flask was kept in the dark and the reaction vessel placed in the cavity of a Rayonet photochemical reactor. In the preliminary experiments the reactor was equiped with 16 lamps (RPR 300 or RPR 253.7nm). In the quantitative experiments only four lamps were fitted. All irradiations were performed at the ambient temperature within the cavity (~30°).

Solvent (Freon 11 or pentane: 10ml) containing a known amount of the internal standard (1a,2: diglyme, 1b: triglyme) was added via a needle valve, both to the reaction vessel and to the reference flask. Further solvent was added while the flask was still under reduced pressure to ensure that all of the internal standard was introduced. The flasks were shaken vigorously for 5 min. and then cooled to -20° for 1 hr. After warming to room temperature the flasks were shaken for a further 10 min., opened to the atmosphere and the mixture analysed by GLC. Between irradiations the flasks were washed thoroughly with Decon 90, rinsed several times with distilled water and dried at 120° for 3 hr.

Actinometry. 2-Hexanone was photolysed as described above, with the exception that benzene was used as internal standard. The light absorbed was calculated from the amount of acetone produced (GLC analysis) and the known vapour-phase quantum yield for the reaction[15]. The amount of light absorbed by the βγ-enones 1a.,1b and 2 was calculated from the relative extinction coefficients in solution (MeOH), and the relative concentrations in the reaction vessel as measured by either use of the reference flask, or measurement of the vapour-pressure.

Flash Vacuum Thermolysis Experiments. The βγ-enone (0.2g) was distilled (Hg diffusion pump) at ambient temperature through a silica tube (10cm or 20cm) heated to 300-500°. The distillate was collected in a U-tube cooled in liquid nitrogen, and analysed by GLC. In the case of 1e the major product was purified by preparative GLC and shown to be identical with an authentic sample of 1-methoxybicyclo[3.2.1]oct-3-en-2-one (19)[10].

Acknowledgement One of us (TJE) is grateful for the award of an SRC (now SERC) Studentship.

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