under aspirator vacuum, and the ethanol was removed under 8-mmHg vacuum. The resulting aqueous slurry was lyophilized to a dry white powder. The product was recrystallized from ethyl acetate to afford 0.170 g (0.295 mmol, 81% yield) of 16$_2$SH,Cl⁻ (**2**): mp 129–132 °C; the free SH activity was 101 ± 2% by Ellman's assay;[25,50] NMR (CDCl$_3$, Me$_4$Si) δ 0.88 (t, 6 H, 2Me), 1.27 (s, 56 H, [(CH$_2$)$_{14}$]$_2$), 3.4 (m, 12 H, (CH$_2$)$_2$N⁺(CH$_3$)CH$_2$CH$_2$SH); the 3 H SCOCH$_3$ singlet of 16$_2$SAc,Cl⁻ (δ 2.37) was absent in the spectrum of 16$_2$SH.

Kinetic Studies. The preparation of 16$_2$SH vesicles is described above (see the Results section). Two-syringe, stopped-flow reactions were followed with a Durrum (Dionex) Model D-130 spectrophotometer fitted with a Beckman DU-2 monochromator. Absorbance data were acquired by a photomultiplier tube linked to a custom-built 2048 channel, adjustable sampling time, A/D converter and thence to a Commodore Model 8032 microcomputer for disk storage. Kinetic analysis with custom-written software and high-resolution graphics employed either the 8032 or (later) a Commodore Model SP9000 "Super Pet" microcomputer. All pH measurements were made with a Radiometer Model 25 pH meter. Details of reagent concentrations, observed rate constants, reproducibilities, and reaction conditions appear in the Results section and in Table II.

Three-syringe, stopped-flow experiments made use of a Dionex Model D-132 multimixing unit, retrofitted to the Model D-110 stopped-flow

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(50) 16$_2$SH that had been oxidized by exposure to air could be restored to quantitative Ellman's activity by recrystallization from ethyl acetate to which a slight excess of dithiothreitol had been added.

spectrophotometer. The data collection and analysis system was unchanged. Results of these experiments appear in Tables III and IV.

Fluorescence Experiments. Static fluorescence measurements were made with a SLM Model 4800 instrument equipped with a Xenon excitation lamp: excitation slit, 8 nm; emission slit, 0.5 nm. Data were collected with an Apple IIe computer and could be corrected for instrument response. Output was digital or analog, as desired.

Stopped-flow fluorescence experiments employed the Durrum Model 110 instrument equipped with a special cuvette designed for emission at 90° to the probe beam. A Corning 3-72, 420-nm cutoff filter was inserted between the sample and the photomultiplier tube to screen out scattered excitation light. UV excitation was provided by an Osram 150-W xenon lamp powered by a Model DCR-150X (Gates and Co.) power supply. The excitation light was passed through a Beckman DU-2 monochromator set at 368 nm. Results of the fluorescence studies appear above and in Table I.

Gas-Phase Photochemistry of a β,γ-Unsaturated Ketone. Concerted and Radical Mechanisms of the 1,3-Acetyl Shift in 1,2-Dimethylcyclopent-2-enyl Methyl Ketone

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Abstract: The 1,3-acetyl shift of the photoexcited β,γ-unsaturated ketone 1,2-dimethylcyclopent-2-enyl methyl ketone has been investigated in the gas phase at room temperature and with 1 bar of CO$_2$ as a buffer gas. Roughly 25% of the total 1,3-acetyl shift reaction is shown to proceed in an orbital-symmetry-allowed concerted fashion from the first excited singlet state. The dominant primary reaction occurs by α-cleavage and recombination of the radicals, as it also does in liquid solution. The effects of radical scavenging and triplet quenching by added NO, O$_2$, and *trans*-1,3-pentadiene served to differentiate between the concerted and radical recombination pathways and between the singlet and triplet excited-state origins of the products. The quenching of the triplet-generated oxa-di-π-methane rearrangement shows that the reaction is initiated in the lowest lying T$_1$ (π,π*) state.

The solution photochemistry of β,γ-unsaturated ketones (β,γ-UKs) has been thoroughly investigated and extensively reviewed in recent years.[1] It is characterized by two reactions: the allylic 1,3-acyl shift (1,3-AS) and the oxa-di-π-methane (ODPM) rearrangement. Photo-CIDNP, stereochemical experiments, and a combination of fluorescence lifetime and reaction quantum yield studies[2a–c] have shown that the S$_1$ photochemistry of a model series of β,γ-UKs, the cyclopent-2-enyl methyl ketones, is dominated by one temperature-activated process leading, in part, to the 1,3-AS. Intersystem crossing populates both T$_2$ (n,π*), which again undergoes the 1,3-AS,[2d] and T$_1$ (π,π*), which affords the

Scheme I. 1,3-AS (→ 2) and ODPM Rearrangement (→ 3) of 1,2-Dimethylcyclopent-2-enyl Methyl Ketone (1)
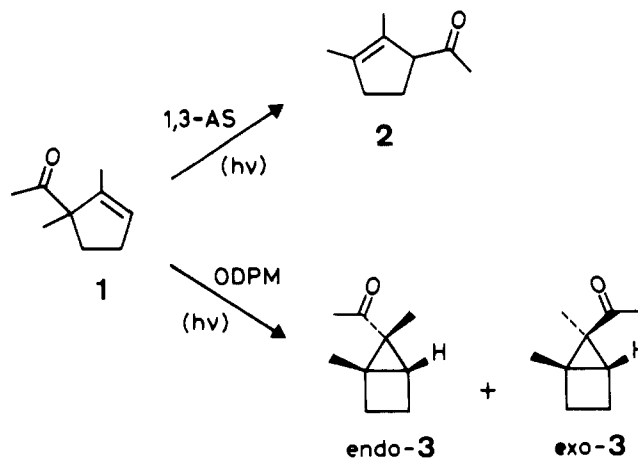
ODPM product.[2d–f] On direct excitation the triplet reactions are only minor processes. For β,γ-UKs other than the above models

(1) Schuster, D. I. In *Rearrangements in Ground and Excited State*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 167.

(2) (a) Henne, A.; Siew, N. P. Y.; Schaffner, K. *J. Am. Chem. Soc.* **1979**, *101*, 3671; *Helv. Chim. Acta* **1979**, *62*, 1952. (b) Sadler, D. E.; Hildenbrand, K.; Schaffner, K. *Ibid.* **1982**, *65*, 2071. (c) Sadler, D. E.; Wendler, J.; Olbrich, G.; Schaffner, K. *J. Am. Chem. Soc.* **1984**, *106*, 2064. (d) Mirbach, M. J.; Henne, A.; Schaffner, K. *Ibid.* **1978**, *100*, 7127. (e) Tegmo-Larsson, I.-M.; Gonzenbach, H.-U.; Schaffner, K. *Helv. Chim. Acta* **1976**, *59*, 1376. (f) Gonzenbach, H.-U.; Tegmo-Larsson, I.-M.; Grosclaude, J.-P.; Schaffner, K. *Ibid.* **1977**, *60*, 1091. (g) Winter, B.; Schaffner, K. *J. Am. Chem. Soc.* **1976**, *98*, 2022. (h) Schaffner, K. *Tetrahedron* **1976**, *32*, 641; *J. Synth. Org. Chem. Jpn.* **1979**, *37*, 893.
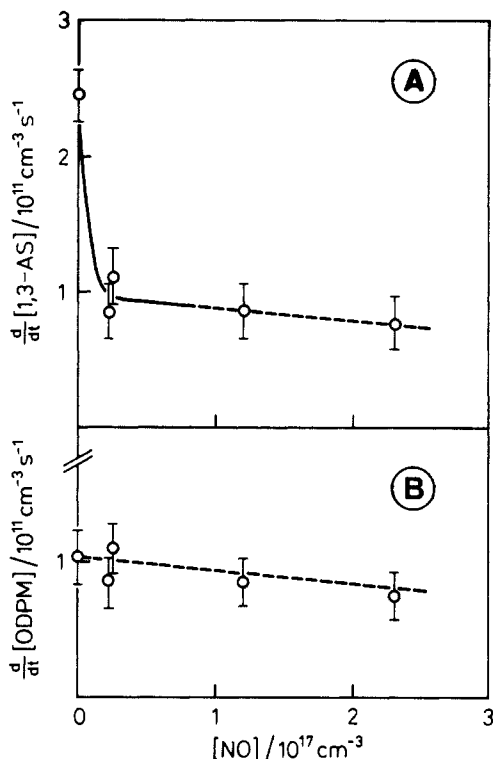
Figure 1. Rates of product formation (A, 1,3-AS to 2; B, ODPM rearrangement to 3) as a function of added NO. The slopes of the broken lines (-----) are uncertain in view of the relatively large error bars. *Note* the different abscissa scales in Figures 1, 2, and 4.

the ODPM rearrangement has been shown to occur in a stepwise fashion, presumably involving biradical intermediates.[2g,3] The 1,3-AS proceeds from both n,π* states[2d,h,4,5] via α-cleavage and radical pair formation.[2a-c,4] The possible additional contribution of an orbital-symmetry-allowed[6] concerted pathway to the 1,3-AS is unproven but suggested by our previous work on the cyclopentenyl ketones.[2c]

We now show that, in the gas phase, roughly 25% of the 1,3-AS of 1,2-dimethylcyclopent-2-enyl methyl ketone (Scheme I: 1 → 2) proceed in a concerted manner and not via radical pairs. The technique employed was static irradiation with gas chromatographic (GC) product analysis, using NO, O_2, and *trans*-1,3-pentadiene as scavengers and CO_2 as a buffer gas.

Experimental Section

Racemic 1,2-dimethylcyclopent-2-enyl methyl ketone (1),[2f] 3-pentanone, and *trans*-1,3-pentadiene (both from Aldrich) were purified by preparative GC to >99.9% purity. The purities of the gases as stated by the manufacturers were CO_2 99.998% (Air liquide), O_2 99.995% (Messer Griesheim), and NO >99.8% (Air liquide). CO_2 and O_2 were used as delivered. NO was passed over Ascarite (Fluka) in order to remove higher oxides.

The irradiation experiments were carried out at room temperature with 1 bar of CO_2 as a buffer gas. Cylindrical quartz cuvettes of 10-cm length and 5-cm diameter, equipped with greaseless stopcocks, served as the reaction vessels. For actinometric purposes the temperature was controlled to ±2 °C. The light of an OSRAM HBO 500W high-pressure mercury lamp was collimated and then filtered through 15 cm of 0.05 M $NiSO_4$ in water, a combination of glass filters (2 mm BG24, 2 mm WG305, and 1 mm UG11, all from Schott), and a Schott UV-IL interference filter centered at 313 nm with a bandwidth of 8 nm fwhm.

(3) Dauben, W. G.; Lodder, G.; Robbins, J. D. *J. Am. Chem. Soc.* 1976, *98*, 3030; *Nouv. J. Chim.* 1977, *1*, 243.
(4) Gonzenbach, H.-U.; Schaffner, K.; Blank, B.; Fischer, H. *Helv. Chim. Acta* 1973, *56*, 1741.
(5) Dalton, J. C.; Shen, M.; Snyder, J. J. *J. Am. Chem. Soc.* 1976, *98*, 5023. Schuster, D. I.; Eriksen, J.; Engel, P. S.; Schexnayder, M. A. *Ibid.* 1976, *98*, 5025. Schuster, D. I.; Calcaterra, L. T. *Ibid.* 1982, *104*, 6397.
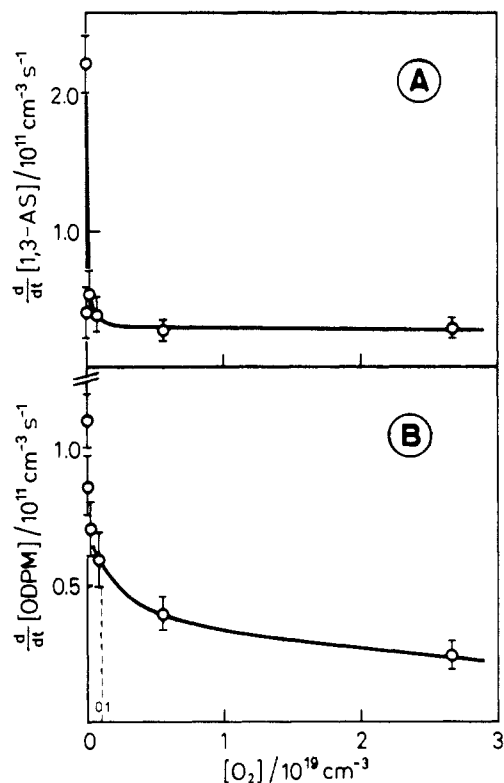(6) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* 1969, *8*, 781.

Figure 2. Rates of product formation (A, 1,3-AS to 2; B, ODPM rearrangement to 3) as a function of added O_2. See also the note to Figure 1.
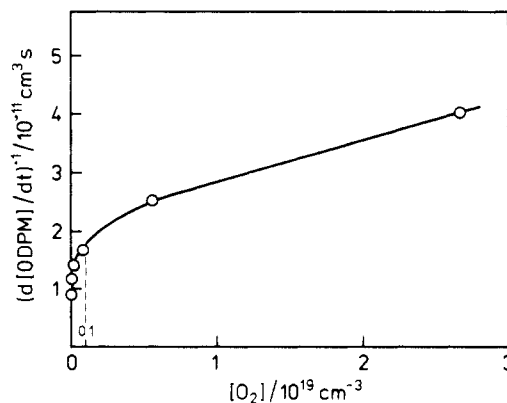

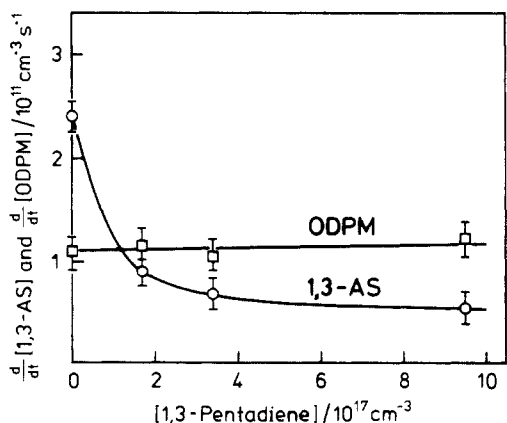Figure 3. Stern-Volmer plot of the formation of the ODPM products *endo*- and *exo*-3. Quencher: O_2.

Figure 4. Effect of added *trans*-1,3-pentadiene on the rates of product formation (A, 1,3-AS to 2; B, ODPM rearrangement to 3). See also the note to Figure 1.

The radiation flux at 313 nm was permanently monitored by a detector unit located behind the irradiation vessel, consisting of a wire mesh
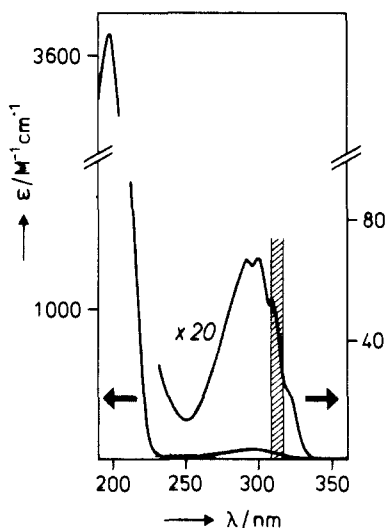
Figure 5. Bandwidth (fwhm) and position of the exciting light (shaded area) within the n → π* absorption band of ketone **1** [gas phase/0.47 torr, 1 bar CO_2, room temperature; the spectrum in the absence of added CO_2 was indistinguishable (instrumental uncertainty ± 1 nm) from the spectrum shown].

attenuator, a narrow-band interference filter at 313 nm, and a photomultiplier. The absolute value of the flux was routinely determined between runs by 3-pentanone actinometry at 130 °C[7] and was found to decrease slowly during the course of the experiments; the average value was ca. 1×10^{15} cm^{-2} s^{-1}.

Since the absorbances of ketone **1** and the 3-pentanone actinometer at 313 nm were very low (<0.05), absolute quantum yield values are not reported. Instead, rates of product formation are given in Figures 1–4.

The relatively low vapor pressure of the starting material at room temperature posed a special problem, affecting the sensitivity of the analytical setup and restricting working pressures to less than about 0.5 Torr.

Absolute pressures of the constituents were measured with calibrated pressure transducers: two fused quartz pressure gauges (Texas Instruments 145-01 and RUSKA DDR-6000), a membrane-type electronic manometer (Datametrics 511-10), and a variable reluctance transducer (Validyne DP-7).

An automatic gas inlet system[8] was used for reproducible sampling. GC analyses were performed on an OV 101 glass capillary column, length 31 m, with a flame-ionization detector coupled to a computer-controlled electronic integrator. The β,γ-UKs **1** and **2**, the ODPM products *endo*- and *exo*-**3**, and the disproportionation and combination products of 1,2-dimethylcyclopent-1-en-3-yl radical were identified by their retention times, known for the same GC system from the preceding investigation.[2c]

Results

When the irradiation of **1** was performed at room temperature in the presence of 1 bar of CO_2, GC analysis showed that the products were those also obtained in the solution experiments,[2f] i.e., the major product **2** resulting from the 1,3-AS, the ODPM products *endo*- and *exo*-**3**, and the products of disproportionation and combination processes of the acetyl and 1,2-dimethylcyclopent-1-en-3-yl radicals.

In the presence of small amounts of NO the rate of the 1,3-AS was strongly reduced. It decreased much more slowly on further NO addition, and approximately 35% of product **2** remained unscavenged (Figure 1A). The ODPM rearrangement was much less affected by small amounts of NO. The rate of formation of **3** decreased only slightly, if at all, with NO pressure (Figure 1B), in a manner similar to that for the 1,3-AS product (**2**) after the initial steep decrease (Figure 1A),

The 1,3-AS initially behaved in a similar fashion on O_2 addition (Figure 2A). Again the rate initially dropped very quickly, but then leveled off completely. Even at the highest O_2 pressure (1

(7) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966; p 782.

(8) Gauthier, M.; Pilon, R.; Kutschke, K. O. *J. Chromatogr. Sci.* **1982**, 20, 283.

Scheme II. Radical-Pair- and Orbital-Symmetry-Controlled Concerted Pathways Available to the 1,3-AS
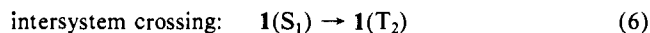

stepwise via radical pair
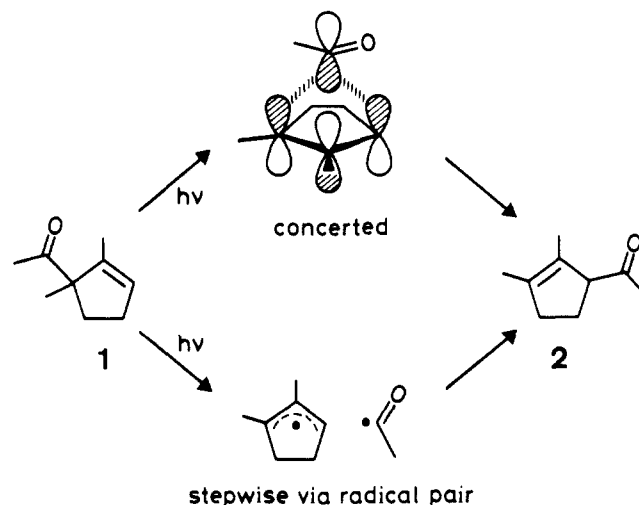
bar) about 15% of the 1,3-AS remained unquenched. The rate of the ODPM rearrangement decreased more gradually (Figure 2B). A Stern–Volmer plot shows curvature at low pressure of O_2 (Figure 3).

In the presence of *trans*-1,3-pentadiene, the 1,3-AS decreased gradually to approximately 25% of the initial value, whereas the ODPM formation remained virtually unaffected within the range of diene concentrations employed (Figure 4).

Discussion

The results of this study are compatible with the reaction steps $1-10^{2c}$ (steps 2 and 3 are not discussed in this work). It is known neither by which mechanism(s) the T_1 and T_2 states return to S_0 (β,γ-UKs of type **1** do not phosphoresce at 77 K[2f]) nor whether energy transfer or chemical scavenging, or both, are involved in the quenching of these states. For this reason such triplet deactivation processes are not included in the scheme below:
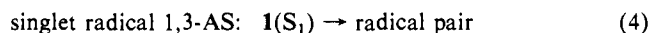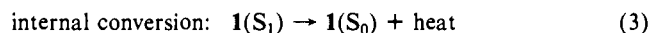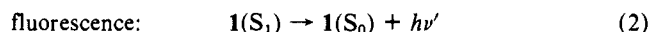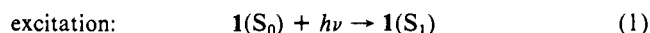
excitation:	$1(S_0) + h\nu \rightarrow 1(S_1)$	(1)
fluorescence:	$1(S_1) \rightarrow 1(S_0) + h\nu'$	(2)
internal conversion:	$1(S_1) \rightarrow 1(S_0) + heat$	(3)
singlet radical 1,3-AS:	$1(S_1) \rightarrow$ radical pair	(4)
concerted 1,3-AS:	$1(S_1) \rightarrow 2$	(5)
intersystem crossing:	$1(S_1) \rightarrow 1(T_2)$	(6)
	$1(S_1) \rightarrow 1(T_1)$	(7)
triplet radical 1,3-AS:	$1(T_2) \rightarrow$ radical pair	(8)
internal conversion:	$1(T_2) \rightarrow 1(T_1)$	(9)
ODPM rearrangement:	$1(T_1) \rightarrow$ biradical	(10)
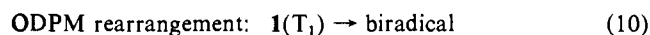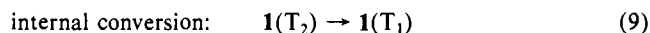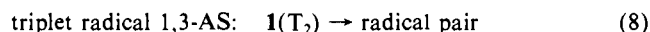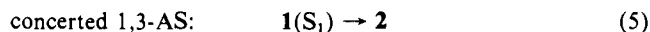
The occurrence of $S_1 \rightarrow T_1$ intersystem crossing (step 7) has not been established in the solution experiments. It must be included, however, in the gas-phase reaction in order to rationalize the curved Stern–Volmer plot in Figure 3.

The 1,3-Acetyl Shift. The gas-phase conditions were chosen in this study in order to screen for any possible orbital-symmetry-controlled[6] concerted pathway for the 1,3-AS **1 → 2**. The use of CO_2 as an inert buffer gas and the selective excitation of the lower vibrational n → π* modes (Figure 5) provided reaction conditions as similar as possible to those in hydrocarbon solution. Thus, preliminary irradiation experiments with CO_2 and Ar[9] as

(9) The experiments with Ar were discontinued because the tendency of **1** to adsorb on the walls was greater than with CO_2.

the buffer gases had afforded identical results, and the $n \rightarrow \pi^*$ absorption band was insensitive to the addition of 1 bar of CO_2 (Figure 5). In the solution experiments, a direct differentiation between a concerted reaction and the rapid primary geminate recombination (10^{-13}–10^{-11} s) of the radical pairs generated from S_1 (Scheme II), which yield at least part of the unpolarized (no CIDNP) 1,3-AS product,[2a-c] had not been possible. Since there are no cage effects in the gas phase, primary and secondary geminate radical recombinations are avoided, and only free radical and unimolecular reactions are encountered. The relatively high pressure of the buffer gas ensured that wall contacts were minimized and all primary photoproducts were vibrationally equilibrated.

In order to assess the importance of a possible contribution from a concerted pathway, the response of the rates of product formation to added NO, O_2, and *trans*-1,3-pentadiene was studied. These gases can act with varying efficiencies both as triplet quenchers and as radical scavengers, with NO being known as the most efficient radical scavenger of the three.[10]

The rapid decrease in 1,3-AS rate in the presence of increasing amounts of NO, O_2, or *trans*-1,3-pentadiene is obviously due to suppression of the radical pathway (Figures 1A, 2A, and 4). *The formation of the remaining, unscavenged part of the 1,3-AS Product (mean value for the three scavengers 25%) can be attributed to the concerted mechanism.* We consider that the dynamic characteristics of this part of the reaction, viz., the fact that a process of this kind is nonscavengeable even under our forcing conditions, is a sufficient experimental criterion for its concerted (one-step) nature, as opposed to primary geminate recombination which is an important contribution in solution.[2c] Complete radical dissociation is expected to occur on a time scale of the order of 10^{-14} s at a collision frequency of ca. 10^{10} s^{-1} at 1 bar total pressure.

Rogers[12] in a recent gas-phase study of the photochemistry of some cyclic β,γ-UKs has also arrived at the conclusion that a concerted mechanism contributes to the 1,3-AS.

The Oxa-di-π-methane Rearrangement. There were very small effects, if any (considering the error bars), on the ODPM rearrangement upon addition of NO (Figure 1B) and *trans*-1,3-pentadiene (Figure 4). The absence of any important scavenging by NO can nevertheless be reconciled with a stepwise ODPM mechanism.[2g,3] At such low NO partial pressures neither the proposed 1,3- and 1,4-biradical intermediates[13] nor any triplet states are expected to be intercepted.

In contrast to the experiments with NO, quenching by ground-state O_2 is unequivocally operating (see the two different slopes in the O_2 concentration ranges above and below ca. 1 × 10^{18} cm^{-3} in Figures 2B and 3), and there are at least two processes which contribute. This is particularly evident from the Stern–Volmer plot in Figure 3. The curved plot can only result from the quenching of two coupled pathways (i.e., quenching of two different triplet states, T_2 and T_1, as they are generated in steps

6 and 7 and 9, respectively) leading to 3. The fast process cannot be quenching of the S_1 state since the O_2 concentration at which reduction of the ODPM reaction is already noticeable is too low. Thus, the lowest O_2 partial pressure employed (1.3 torr O_2) already roughly halves the ODPM yield quenchable by the fast process. Yet, the calculated collisional lifetime of 1 with respect to O_2 is as short as $\tau_{coll(O_2)}$ ca. 20 ns, whereas the S_1 lifetime in liquid solution is ca. 0.5 ns[2c] and should be even shorter in the gas phase in the absence of cage effects. The steep initial slope must therefore involve quenching of either T_2 or a combination of T_1 and T_2, while another component responsible for the flattening of the curve can be attributed to quenching of either the T_1 state or a biradical leading to the ODPM rearrangement.[14] That quenching of T_2 (n,π^*) is the fast process is backed up by the observation that the unquenched portion of the 1,3-AS is smaller in O_2 (Figure 2A) than in either NO or 1,3-pentadiene (Figures 1A and 4, respectively) at similar concentrations.

The observation that the ODPM rearrangement of 1 is not quenched by 1,3-pentadiene upon direct excitation could be construed as evidence that the reaction occurs from an excited state higher than T_1 (π,π^*), i.e., from either the T_2 or S_1 n,π^* state.[15] However, our gas phase results are only compatible with T_1 (π,π^*) as the ODPM-reactive state. On the one hand, the direct evidence from liquid-phase experiments assigning the 1,3-AS and ODPM reactions of the cyclopentenyl methyl ketones to the n,π^* and π,π^* states, respectively, appears unequivocal,[2a,c-f,h] and it is likely that reversing this reactivity–electronic configuration relationship would require a larger perturbation of the β,γ-UK system than the mere change from hydrocarbon solution to the gas phase. On the other hand, the energy difference between T_1 and T_2 is very small in solution, and the ordering could well invert as a result of subtle changes in structure and environmental influences. However, an evaluation of the quenching results with O_2 leads to the conclusion that the triplet state levels of 1 are not, in fact, inverted in the gas phase. The Stern–Volmer curve of Figure 3, which is composed of two quenchable components (i.e., quenching of T_2 + either quenching of T_1 or scavenging of a biradical intermediate), is only compatible with the ODPM rearrangement occurring from T_1. If the ODPM rearrangement were initiated in the T_2 state, then quenching of either T_1 or T_2, or both, would result in a linear Stern–Volmer plot.[16]

(10) Scavenging rate constants for methyl radicals by NO, O_2, and ethene are 1.1 × 10^{-11}, 1.2 × 10^{-12}, and 2 × 10^{-15} cm^3 s^{-1}, respectively (at room temperature and 700 torr N_2).[11] Our results suggest that 1,3-pentadiene should be more reactive than ethene by about one order of magnitude.

(11) *NBS Spec. Publ.* **1977**, *513. NSRDS-NBS* **1980**, *67*.

(12) Eckersley, T. J.; Rogers, N. A. J. *Tetrahedron* **1984**, *40*, 3759.

(13) Scaiano, J. C. *Acc. Chem. Res.* **1982**, *15*, 252.

(14) It is not possible to differentiate between energy transfer and chemical scavenging as the quenching mechanisms of T_1 and T_2, since the rate constants of bimolecular reaction and energy transfer are estimated to be of the same order of magnitude, taking 3.4 and 6 Å for the diameters of O_2 and 1, respectively, and [O_2] = 1 × 10^{18}–3 × 10^{19} cm^{-3} as well as appropriate quenching rate constants of O_2 from Gijzeman et al. [Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc. Faraday Trans. 2* **1973**, *69*, 708].

(15) Compare the suggestion by Rogers (ref 12 and Eckersley, T. J.; Parker, S. D.; Rogers, N. A. J. *Tetrahedron* **1984**, *40*, 3749) that the ODPM rearrangement of bicyclo[2.2.2]octenones may not always be initiated in the lowest lying triplet state.

(16) No quenching was detected in exploratory experiments in liquid cyclohexane solutions with *trans*-1,3-pentadiene concentrations ≤4 × 10^{-3} M, i.e., about twice the maximum concentration used in the gas phase. This surprising failure of quenching by diene is under further study.