occurred at −1.7 eV vs. Ag quasi-reference electrode, implying that oxidation by Cd(II) should occur readily. The possibility of ring opening by further photoinduced reduction of **3** to a radical dianion is unlikely in view of this potential. Although Newcomb et al. have shown that opening by a radical anion route occurs rapidly if a neutral aryl cyclopropane is treated with strong base,[16] this route to ring-opened product appears to be unimportant if **3** is generated with lithium diisopropylamide. **3** can be essentially quantitatively methylated if the solution of **3** in THF is quenched by methyl iodide.[17]

(15) Cd(II) has been used previously in oxidative dimerization of anions: Harvey, R. G.; Cho, H. *J. Am. Chem. Soc.* **1974,** *96,* 2434.

(16) Newcomb, M; Seidel, T.; McPherson, M. B. *J. Am. Chem. Soc.* **1979** 101, 777.

(17) Boche, G.; Martens, D. *Angew. Chem., Int. Ed. Engl.* **1972,** 11, 724.

(18) A ^{1}H NMR spectrum of the dimeric fraction (*m/e* 438) exhibited signals in the vinylic region.

(19) Upon photoexcitation, **9** reacts at least three times more slowly than does **3**, despite the similarity of their absorption spectra. The absence of red color in the photolysis mixture indicates that its disappearance proceeds through intermediates different from **4** and/or **5**.

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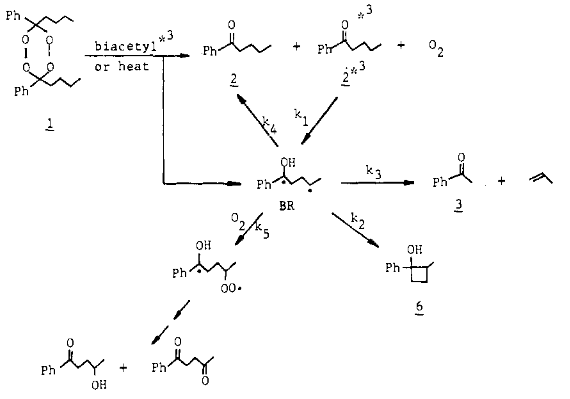
Received February 26, 1979

Formation of the Norrish Type II Products from the Biacetyl-Sensitized Photolysis of Valerophenone Diperoxide

Sir:

In connection with the chemistry of high-energy-content molecules which contain an intramolecular probe for excitation,[2] we have recently reported[1b] that the triplet excited state of valerophenone (**2**) may be formed by the thermal and biacetyl-sensitized decomposition of valerophenone diperoxide (**1**) (eq 1). We now report evidence that acetophenone (**3**), one of the Norrish type II products of **2**,[3] comes from a 1,4 biradical (BR) which is formed directly by the biacetyl-sensitized decomposition of **1** without going through triplet valerophenone.



(1)

The type II reaction of **2** in benzene is known to occur from the triplet n,π* excited state of **2** to produce exclusively the 1,4 biradical ($k_1 \sim 1.3 \times 10^8\ \mathrm{s}^{-1}$) which (a) disproportionates back to **2** ($k_4 \sim 1.8 \times 10^7\ \mathrm{s}^{-1}$), (b) fragments to **3** and propylene ($k_3 \sim 1 \times 10^7\ \mathrm{s}^{-1}$), or (c) closes to form 2-methyl-1-phenylcyclobutanol (**6**) ($k_2 \sim 0.2 \times 10^7\ \mathrm{s}^{-1}$).[3]

A solution of **1**[4] in benzene ($\sim 10^{-2}$ M) containing various concentrations of biacetyl as a sensitizer (0.01–2.3 M) was irradiated with light of >400-nm wavelength under bubbling nitrogen to give valerophenone (**2**), acetophenone (**3**), γ-hydroxyvalerophenone (**4**), 1-phenylpentane-1,4-dione (**5**), and biphenyl (Table I) in addition to a small yield of butyl benzoate (<5%).[5] In a separate experiment all of these products were isolated and identified by direct comparisons with authentic samples. Traces of phenyl valerate could occasionally be detected (<2%).

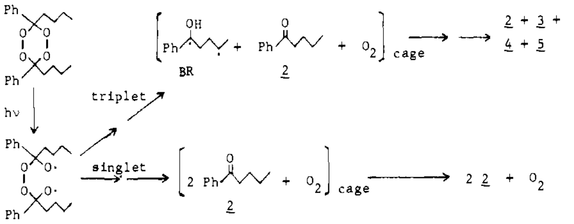
Table I. Biacetyl-Sensitized Photolysis of Valerophenone Diperoxide (**1**) in Benzene[a]

biacetyl, M	irradn time, h	products, %[b,c]					recovd **1**, %[b]
		2	**3**	**4**	**5**	Ph_2	
0.010	18	15	9	6	11	25	83
0.034	10	23	15	5	17	31	82
0.225	10	27	24	5	10	19	74
0.46	11	29	33	8	13	10	76
1.15	8	20	27	9	8	3	76
2.30	8.5	12	22	7	7	2	75

[a] Irradiations were carried out with a 400-W high-pressure mercury lamp through a 10% sodium nitrite solution (>400 nm) at room temperature under bubbling nitrogen which was deoxygenated by passing through an alkaline pyrogallol solution. A control experiment was done in every case. [b] Estimated errors ±50%. [c] The yield of 2-methyl-1-phenylcyclobutanol (**6**) was negligibly small.[7]

It should be noted that the yield of **3** did not decrease or even increase with increasing concentration of biacetyl, indicating that triplet valerophenone is not a precursor of **3**. The biacetyl would have quenched any triplet valerophenone, since $k_q(\mathbf{2}^{*3} \rightarrow \text{biacetyl}) \sim 1.5 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ in benzene.[6]

Our VPC showed that there was formed only a negligible amount of the other type II product (**6**).[7] However, we believe that **3** was formed via the 1,4 biradical, since **4** and **5** were produced simultaneously with **3**. The production of **4** and **5** can be rationalized by assuming that BR is trapped in a solvent cage with oxygen which may be formed together with BR from the decomposition of the peroxide **1** (eq 2a).[8] Recently Small and Scaiano[9] have shown that oxygen interacts with the 1,4 biradical with $k_5 \sim 8.4 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ in benzene. As was suggested by them,[9] we found that irradiation of **2** in benzene under bubbling oxygen, followed by treatment of the reaction mixture with triphenylphosphine, produced **4** (7%) and **5** (0.5%) along with **3** (83%) and **6** (9%).[10]



(2a)

(2b)

The intermediacy of the biradical in the biacetyl-sensitized photolysis of the peroxide **1** also seems corroborated by the effect of alcohol; the quantum yield of **3** from the sensitized photolysis of **1** in benzene increased with increasing concentration of added *tert*-butyl alcohol or 3-ethyl-3-pentanol, as is expected from Wagner's report.[11,12]

Biphenyl quenches biacetyl phosphorescence inefficiently with $k_q(\text{biacetyl}^{*3} \rightarrow \text{biphenyl}) \sim 3.2 \times 10^3\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ in benzene[6] and quenches the type II reaction of **2** efficiently with $k_q(\mathbf{2}^{*3} \rightarrow \text{biphenyl}) \sim 1.4 \times 10^9\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ in benzene.[6] The formation of **3** from the biacetyl-sensitized photolysis of **1** in benzene (0.11 or 0.057 M biacetyl) was somewhat quenched by diphenyl (0.05–0.5 M), and the quenching data are totally explicable in terms of the quenching of triplet biacetyl,[13] not triplet valerophenone. It is now quite reasonable to conclude (1) that the decomposition of peroxide **1** is initiated by triplet biacetyl to result in the efficient formation of **3** without the

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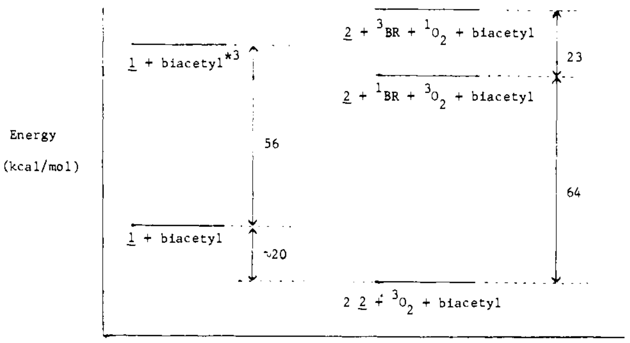


Figure 1. Energy diagram for the conversion **1** + biacetyl^{*3} → **2** + BR + O_2 + biacetyl.[14]

intermediacy of triplet valerophenone; and (2) that the 1,4 biradical is most probably a precursor of **3**.

Another striking feature of the results in Table I is that the distribution of products **3–6**, all of which can be ascribed to BR (eq 1), is definitely different from that obtained from the photolysis of **2** in benzene in the absence[3,11] or presence[9] of oxygen. From consideration of spin selection and the energetics of the conversion **1** + biacetyl^{*3} → **2** + BR + O_2 + biacetyl, the multiplicities of BR and O_2 seem to be singlet (^{1}BR) and triplet ($^3O_2$), respectively (Figure 1).[14] Formation of ^{3}BR and $^1O_2$ seems energetically difficult. If this assumption holds true, BR derived from the decomposition of **1** (^{1}BR) can be distinguished from the type II 1,4 biradical, which is initially produced in a triplet state (^{3}BR). This difference in the BR multiplicity may explain why, in the case of the biacetyl-sensitized decomposition of **1**, the yield of **6** is unusually small.[18] The much larger yields of γ-oxidation products **4** and **5** from **1** than expected from Scaiano's spin statistical consideration[9,20] may be due to the simultaneous occurrence of the reaction 3.[8] We must conduct further quantitative experiments to clarify these problems, because the biacetyl-sensitized decomposition of **1** is fundamentally different from the photolysis of **2** in that BR, O_2, **2**, and/or biacetyl would be within the same solvent cage at the moment of their production by the fragmentation of **1**.[21]

Direct irradiation of **1** in hexane ($\sim 10^{-2}$ M) under bubbling nitrogen was carried out at 254 nm to give **2** (29%), **3** (41%), and the cyclobutanol **6** (5%) as the major products. Since **4** and **5** could not be detected in the reaction mixture, in sharp contrast to the biacetyl sensitization (Table I), **3** must have been formed by the direct photolysis of **2** which had escaped from the solvent cage. Alternatively, singlet-sensitized decomposition of **1** by pyrene in benzene (2.9×10^{-2} M pyrene, >350-nm irradiation wavelength) gave **2** (95%) but only a small yield of **3** (<2%). Pyrene is known to act as a singlet sensitizer for the decomposition of tetramethyldioxetane.[22] The fluorescence of pyrene was found to be quenched by **1** with $k_q\tau \sim 14$ M^{-1} in benzene. These facts lead us to conclude that a major decomposition path from the T_1 state of **1** (biacetyl sensitization) is eq 2a and one from the S_1 state of **1** (direct irradiation and pyrene sensitization) is eq 2b.

Acknowledgment. We are sincerely grateful to Professor Peter J. Wagner for his valuable comments. We also thank Mr. Y. Umehara for his technical assistance in preparation of some compounds. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

References and Notes

(1) (a) Photoinduced Reactions. 108. (b) Y. Ito, M. Konishi, and T. Matsuura, *Photochem. Photobiol.*, in press.

(2) T. R. Darling and C. S. Foote, *J. Am. Chem. Soc.*, **96**, 1625 (1974); C. S. Foote and T. R. Darling, *Pure Appl. Chem.*, **41**, 495 (1975); E. J. H. Bechara, A. L. Baumstark, and T. Wilson, *J. Am. Chem. Soc.*, **98**, 4648 (1976). For general chemical titration, see W. Adam, C. Cheng, O. Cueto, K. Sakanishi, and K. Zinner, *ibid.*, **101**, 1324 (1979).

(3) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971); P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **94**, 7495 (1972); R. D. Small, Jr., and J. C. Scaiano, *Chem. Phys. Lett.*, **50**, 431 (1977).

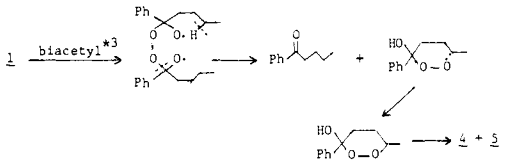
(4) A higher melting isomer of **1**[1b] was used throughout this work. Two butyl groups of this isomer were found to be trans to each other (Y. Ito, H. Yokoya, and T. Matsuura, unpublished work).

(5) Product analyses were done by vapor phase chromatography (VPC) and high pressure liquid chromatography (LC). A 3-m by 4-mm VPC column containing either 20% Carbowax 20M on Celite 545 or 20% silicone DC 550 on Celite 545 was used for the analyses of **2–6**, biphenyl, butyl benzoate, and phenyl valerate. Two LC columns (JASCOSIL WC-01 and JASCOSIL SS-05) were used for the analyses of **1–3**, butyl benzoate, and phenyl valerate. Obviously, the solvent benzene participates in the production of biphenyl, since it was not detected when hexane was used as a solvent. In the previous paper[1b] the yield of butyl benzoate was reported to be higher than the actual value because of the overlapping of its VPC retention time with that of **4**.

(6) The term $k_q(D^* \rightarrow A)$ means a rate constant for the quenching of the excited state of D by the ground state of A. These rate constants were assessed by the standard Stern–Volmer quenching experiments assuming that the lifetime of the triplet state of **2** is 7.6 ns and that of biacetyl 10^{-3} s. The value of $k_q(\text{butyrophenone}^{*3} \rightarrow \text{biphenyl})$ was reported to be 2×10^9 M^{-1} s^{-1} in good agreement with ours (P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2820 (1967)).

(7) Since the cyclobutanol **6** was stable under our reaction conditions, this result is probably due to the small value of $k_2/(k_2 + k_3 + k_4)$ under our reaction conditions. In a separate experiment which was done to a high conversion, we could detect traces of **6** (~0.1%) after the separation of the reaction mixture by a preparative thin layer chromatography.

(8) A referee has indicated another mechanism for the formation of **4** and **5** (eq 3).



(3)

(9) R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, **100**, 4512 (1978).

(10) We did not attempt to isolate γ-hydroperoxyvalerophenone (**7**), the expected precursor of **4** and **5**, but found from the analysis of the photooxidation products of **2** that **7** decomposed to **4** and **5** in good yields on extended irradiation or under the VPC conditions which we used for the analysis of **4** and **5**.

(11) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5898 (1967); P. J. Wagner and I. E. Kochevar, *ibid.*, **90**, 2232 (1968); P. J. Wagner, I. E. Kochevar, and A. E. Kemppainen, *ibid.*, **94**, 7489 (1972).

(12) For example, the quantum yield of acetophenone formation from 0.01 M **1** and 0.1 M biacetyl increased to 1.2 times that in pure benzene by the addition of 1 M *tert*-butyl alcohol. The effects of the alcohol is rather small, compared with the case of the photolysis of **2** (0.1 M in benzene), where the quantum yield of **3** increased by a factor of 2.1.[11] This discrepancy may have something to do with the fact that the type II reactions from the alkyl ketone singlet states are little affected by polar solvents.[19]

(13) We have recently shown[1b] that the triplet state of biacetyl is responsible for the photosensitized decomposition of the peroxide **1**. This was further confirmed by measurements of the quantum yield (Φ) of disappearance of **1** as a function of the concentration of **1**. The value of Φ was $\sim 10^{-3}$ at 0.01 M **1** and 0.11 M biacetyl in benzene. Since the efficiency of energy transfer from the triplet biacetyl to **1** is ~50% under the reaction conditions, the low quantum yield should be due to the ineffectiveness of the bond-cleavage and -forming step.

(14) The energy of BR was estimated by Lewis and Hilliard.[15] The energy of a 1,4-biradical singlet derived from the type II reaction of butanol was estimated by Dewar and Doubleday[16] to be 0.3 kcal/mol lower than that of the corresponding biradical triplet. The reaction enthalpy for the conversion **1** → 2 **2** + $^3O_2$ was estimated to be −11 kcal/mol by Benson's rule,[17] neglecting all corrections for nonbonding interactions. Therefore, its true reaction enthalpy seems more positive than −20 kcal/mol.

(15) F. D. Lewis and T. A. Hilliard, *J. Am. Chem. Soc.*, **94**, 3852 (1972).

(16) M. J. S. Dewar and C. Doubleday, *J. Am. Chem. Soc.*, **100**, 4935 (1978).

(17) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Sham, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969); H. K. Eigenmann, D. M. Golden, and S. W. Benson, *J. Phys. Chem.*, **77**, 1687 (1973).

(18) It is known that the singlet excited state of alkyl ketones gives much less cyclobutanols than the corresponding triplet excited state.[19]

(19) J. C. Dalton and N. J. Turro, *Annu. Rev. Phys. Chem.*, **21**, 499 (1970).

(20) R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, **81**, 2126 (1977).

(21) We have some data that solvent viscosity and reaction temperature considerably change the product yields from **1**.

(22) W. J. Baron and N. J. Turro, *Tetrahedron Lett.*, 3515 (1974).

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Received January 2, 1979