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CHEMILUMINESCENCE ASSOCIATED WITH SINGLET OXYGEN CLEAVAGE OF CYCLOPROPENES; THE DIOXETANES DERIVED FROM TRI- AND TETRAPHENYLCYCLOPROPENE

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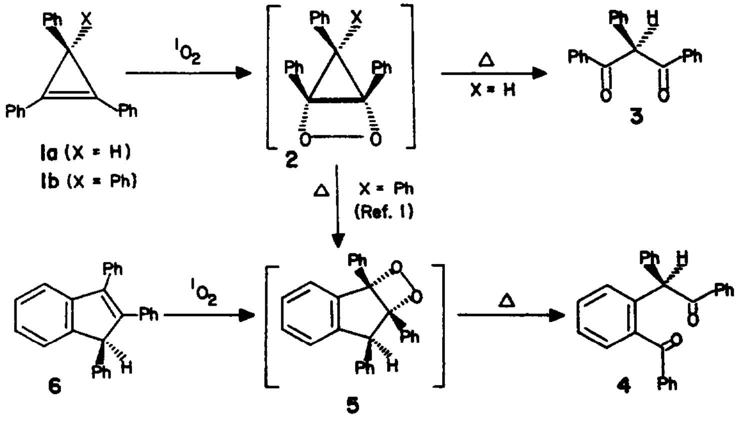
INTRODUCTION

Griffin[1] as well as Schlessinger[2] and their respective co-workers have demonstrated that 1,2-diarylsubstituted cyclopropenes and cyclobutenes, respectively, are vulnerable to attack by photogenerated singlet oxygen[3] and give as isolable products bis diaryl ketones. It is presumed that the initial step in these cleavage reactions is 2 + 2 cycloaddition of singlet oxygen to form transient dioxetanes possessing exceptional strain.[4] Our original work in this area[1] was initiated to determine the nature of the primary oxidation products and to assess the possibility that collapse of dioxetanes derived from strained alkenes might be accompanied by chemiluminescence, *i.e.*, that the ketonic products would be formed in their excited states.

The reactions of 1a and 1b with singlet oxygen lead to remarkably contrasting results (shown below): 1a (X = H) gives the dione 3, a product which is unexceptional based on the reasonable intermediacy of the 1,2-dioxetane 2a; however, 1b (X = Ph) is converted to the rearranged dione 4. A rearrangement of 2b to 5 was proposed to explain this result.[1] Although plausible, *a priori*, it is not obvious why such a process should be effective in competing with the available ring opening of 2b to a 1,3-dione. We report here results which define both 2a and 5 as experimentally detectable species and which confirm the reaction pathways depicted below for the observed reactions 1a + $^1O_2$ → 3 and 1b + $^1O_2$ → 4.



ENERGETIC CONSIDERATIONS

Based on the phosphorescence spectrum of 3 (77°K, 3-methylpentane, 0,0 ∿ 410 nm) the triplet energy (E_T) of 3 (and presumably of 4 also) is expected to be ∿ 70 kcal/mol. The reaction enthalpy for the conversions of 2a → 3 and 5 → 4 may be estimated by group additivity relationships. Both a simple calculation based on bond energies[5] or a more detailed calculation based on heats of formation yield similar estimates (values in kcal/mol):

			Bond Energies	Heats of Formation	E_T of Dione
2a → 3	ΔH	=	∿ 100	100	70
5 → 4	ΔH	=	∿ 100	75	70

It thus appears that both conversions (2a → 3* and 5 → 4*) are *exothermic*. In other typical dioxetane systems studied, an *endothermic* process is involved in excited state formation and *activation energy* is required to achieve reaction and a part of this energy is stored in the chemical potential of the excited state product. Hence, 2a → 3* and 5 → 4* conceivably represent examples of "energy sufficient" exothermic chemiluminescent reactions. Thus it was of interest to determine (a) whether the dioxetanes 2 and 5 are true intermediates as shown above; (b) if 2 and 5 are implicated, whether collapse to 3 and 4, respectively, is accompanied by chemiluminescence; (c) if the answer to questions (a) and (b) is affirmative, what are the activation energies for the chemiluminescent reactions 2 → 3* and 5 → 4*. We report here experimental findings which allow definitive answers to be given to questions (a), (b), and (c).

EXPERIMENTAL RESULTS

Samples of triphenylcyclopropene (1a)[6a] were treated at -77°C with either phospha[3.8.9]-triooxaadamantane ozonide[6b] or triphenylphosphite ozonide[7] in methylene chloride-chlorobenzene, which gives the diketone 3 identified by ir and previously reported as the photooxidation product upon warming to room temperature.[1] The phosphorescence quantum yield of 3 was found to be exceedingly low under our reaction conditions; therefore, indirect probes (triplet-singlet energy transfer acceptors) were employed to monitor production of excited states. In the presence of 9,10-dibromo- or 9,10-diphenylanthracene (DBA and DPA, respectively), or perylene (P), chemiluminescence is observed upon warming the reaction mixture to room temperature which is identical to the *fluorescences* of these energy acceptors. This result requires the presence of an electronically excited species in the reaction mixture capable of transferring energy to the singlet states of DBA, DPA, or P. Treatment of 1a with singlet oxygen produced by photosensitization (polymer-based rose bengal)[6b] followed by removal of sensitizer at -43°C gave a solution containing a species also capable of exciting DBA, DPA, and P. In view of these results, the novel dioxetane 2a is proposed as the most reasonable candidate responsible for the chemiexcitation processes observed.

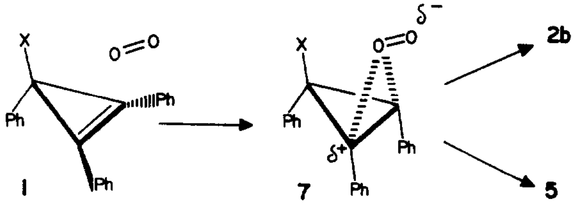
Treatment of 1b[8] with singlet oxygen unexpectedly does not give the anticipated 1,3-dione, but leads instead to the rearranged product 4. Prior rearrangement of 2b to 5 followed by ring-cleavage to 4 was proposed as a mechanism for the interconversion.[1] This proposal was confirmed by generation of 5 from 6 by an alternate route, namely addition of singlet oxygen to 6.[1] That a common dioxetane is produced from both 1b and 6 was confirmed by chemiluminescence techniques. Identification of the common dioxetane was achieved by quantitative comparison of Stern-Volmer plots and of the relative yields of the indirect chemiluminescence ratios obtained from DBA and DPA.[9] From the equivalence of the emission and Stern-Volmer ratios obtained from 1b and 6 with singlet oxygen, it is evident that a common intermediate is responsible for the chemiexcitation steps. Solutions containing the active transient(s) were prepared from 1b and 6 by treatment with triphenyl phosphite ozonide in methylene chloride at $-23^{o}C$ at which temperature the thermolabile dioxetane is indefinitely stable ($K_{decay} = 4.9 \times 10^{-4}\ sec^{-1}$ at $29.5^{o}C$).

Thus, the answers to questions (a) and (b), as posed in the introduction, are convincingly answered in the affirmative. We turn now to the measurement of the value of E_{act} for the chemiluminescent reactions 2a → 3* and 5 → 4*. The temperature coefficient of chemiluminescence (E_{CL})produced in both reactions is readily measured by a step function analysis,[4] and the following results were obtained:

$$\underline{1a} + {}^{1}O_2 \rightarrow \underline{3}^* \qquad E_{CL} = 13\ \text{kcal/mol}$$
$$\underline{1b} + {}^{1}O_2 \rightarrow \underline{4}^* \qquad E_{CL} = 18\ \text{kcal/mol}$$
$$\underline{6} + {}^{1}O_2 \rightarrow \underline{4}^* \qquad E_{CL} = 18\ \text{kcal/mol}$$

The identity of the values of E_{CL} for reaction of both 1b and 6 with singlet oxygen define the reorganization of 5 to 4 as the rate determining step in the conversion of 1b to 4, since this represents the only plausible common step in the reaction pathways (the reaction of singlet oxygen with alkenes requires activation energies of the order of 5 kcal/mol or less).[10]

If 2b is formed along the pathway from 1b to 4, the activation energy of rearrangement of 2b to 5 must be smaller than ∿ 13 kcal/mol (the activation energy for rearrangement of 2a to 3). The observation that 2b reacts much more slowly with ${}^{1}O_2$ than does 2a provides an explanation for the formation of 5 without passing through 2b. Addition of singlet oxygen to alkenes is expected to yield a perepoxide (or open zwitterion equivalent) represented by 7.



The transition state for addition of ${}^{1}O_2$ is more difficult to achieve when X = Ph than when X = H. This explains the slower rate of addition of ${}^{1}O_2$ to 1b relative to 1a. Furthermore, the intermediate perepoxide 7 (X = Ph) will be more prone to undergo reactions competitive with ring expansion to a dioxetane than will 7 (X = H). Also, to the extent that an acyclic zwitterion is involved, cyclopropane ring-opening should be more facile for 7 (X = Ph) than 7 (X = H) because of increased electronic driving force (carbonium ion stability) and release of strain.

SUMMARY

Chemiluminescence techniques have been employed to investigate the basis for the dramatic dichotomy observed in product formation in the reaction of $^1O_2$ with 1a (which undergoes an unexceptional oxidation of the cyclopropene double bond) and with 1b (which leads to an oxidative rearrangement). The dioxetanes 2a and 5 are established as intermediates in reactions 1a + $^1O_2 \rightarrow 3$, 6 + $^1O_2 \rightarrow 4$ and 1b + $^1O_2 \rightarrow 4$. The activation energies for the chemiluminescent ring scissions of 2a $\rightarrow 3^*$ and 5 $\rightarrow 4^*$ have been measured and are found to be $\sim$ 13 kcal/mol and $\sim$ 18 kcal/mol, respectively. A rationale for the diverging pathways for reaction of 1a and 1b with $^1O_2$ is presented. Preliminary experiments with diarylcyclobutenes indicate that they behave in a similar fashion and the results will be reported in a subsequent communication.

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REFERENCES

1. I.R.Politzer and G.W.Griffin, Tetrahedron Lett., 4775 (1973).
2. A.G.Schultz and R.H.Schlessinger, Tetrahedron Lett., 2731 (1970).
3. I.R.Politzer, G.W.Griffin, and J.L.Laseter, Chem.-Biol.Interactions, 3, 73 (1971).
4. (a)N.J.Turro, P.Lechtken, N.E.Schore, G.Schuster, H.-C.Steinmetzer, and A.Yekta, Accounts Chem.Res., 7, 97 (1974); (b) J.W.Hastings and T.Wilson, Photochem.Photobiol., 23, 461 (1976).
5. (a) S.W.Benson, F.R.Cruickshank, D.M.Golden, G.R.Haugen, H.E.O'Neal, A.S.Rodgers, R.Shaw, and R.Walsh,Chem.Rev., 69, 279 (1969); (b) H.E.O'Neal and W.H.Richardson, J.Am.Chem. Soc., 92, 6553 (1970).
6. (a) R.Breslow and H.W.Chang, J.Am.Chem.Soc., 83, 2367 (1961); R.Breslow and P.Dowd, ibid., 85, 2729 (1963); (b) A.P.Schaap, A.L.Tayer, and K.Kees, J.Org.Chem., 40, 1185 (1975).
7. R.W.Murray and M.L.Kaplan, J.Am.Chem.Soc., 91, 5358 (1969).
8. B.Halton, M.Kulig, M.A.Battiste, J.Perreten, D.M.Gibson, and G.W.Griffin, J.Am.Chem.Soc., 93, 2327 (1971). We wish to thank Professor Battiste for supplemental samples of this hydrocarbon.
9. T.Wilson and A.P.Schaap, J.Am.Chem.Soc., 93, 4126 (1971); H.-C.Steinmetzer, A.Yekta, and N.J.Turro, ibid., 96, 282 (1974).
10. R.D.Ashford and E.A.Ogryzlo, J.Am.Chem.Soc., 97, 3604 (1975).
11. (a) M.J.S.Dewar and W.Thiel, J.Am.Chem.Soc., 97, 3978 (1975); M.J.S.Dewar, A.C.Griffin, W.Thiel, and I.J.Turchi, ibid., 97, 4439 (1975).; (b) S.Inagaki and K.Fukui, J.Am.Chem. Soc., 97, 7480 (1975) and Bull.Chem.Soc.Japan, 46, 2240 (1973).