

CYCLOELIMINATION REACTIONS OF CYCLIC ARYL PINACOL SULFITES AND CARBONATES VIA PHOTSENSITIZED REVERSIBLE ELECTRON TRANSFER

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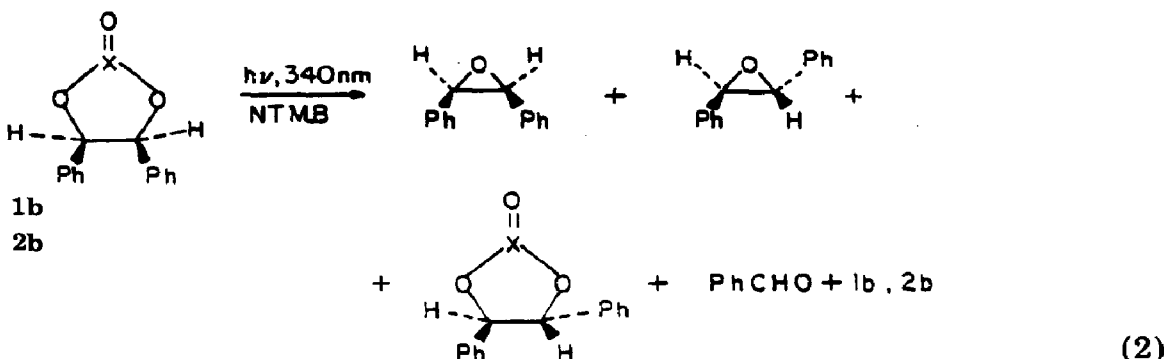
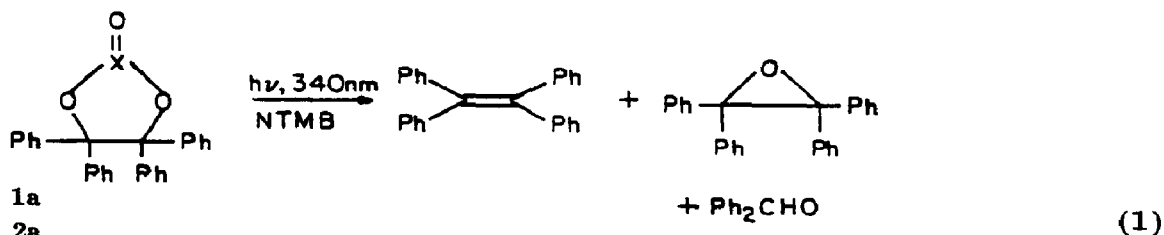
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Summary

Evidence is presented that the singlet and triplet photosensitized cycloelimination reactions of cyclic aryl pinacol sulfites and carbonates proceed by reversible electron transfer and yield products which are different from those formed on direct photolysis.

1. Introduction

Direct irradiation of the cyclic aryl pinacol sulfites **1a** and **1b** ($X \equiv S$) and carbonates **2a** and $2b$ ($X \equiv C$) has been reported to yield arylcarbenes via formal $5 \rightarrow 2+2+1$ cycloelimination [1, 2]:



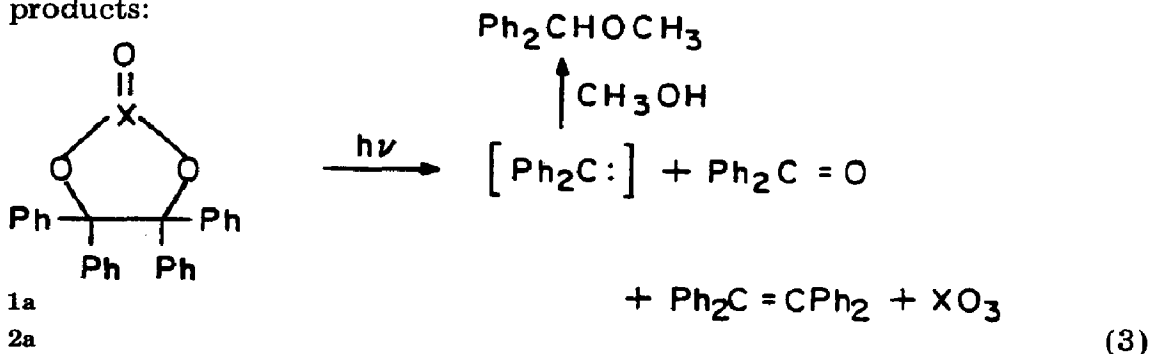
(Ph \equiv phenyl; NTMB \equiv *N,N,N',N'*-tetramethyl benzidine). The reactions of the arylcarbenes generated in this manner were found to be almost identical with those produced by conventional procedures, such as photolysis of aryl-oxiranes and aryl-diazomethanes. Although reactions of 1 and 2 could not be induced by photosensitization via triplet energy transfer, we find that the NTMB is able to photosensitize the cycloelimination reactions of 1 and 2, that a different product distribution is produced by NTMB photosensitization and that the mechanism probably involves reversible electron transfer.

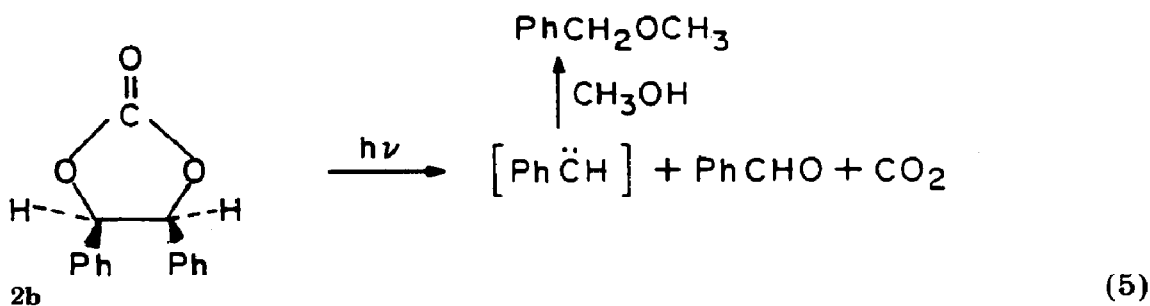
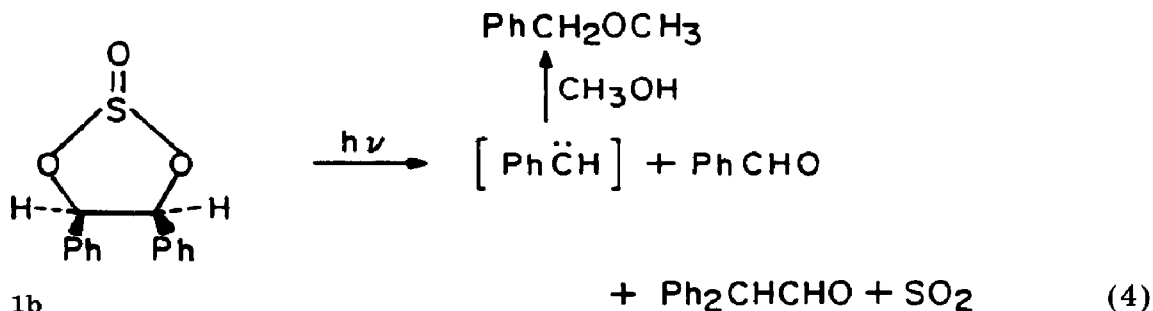
2. Results

The photosensitized reactions were conducted in dry deaerated solutions of acetonitrile containing 0.005 M NTMB and 0.01 M 1 or 2. Irradiations were performed using an excitation wavelength of 340 nm. The yields of products were nearly quantitative (greater than 95%) for each substrate. For 1a and 2a (eqn. (1)) tetraphenylethylene and tetraphenyloxirane were the only detectable products. For 1b [3] and 2b (eqn. (2)), *cis*- and *trans*-2,3-diphenyloxiranes, diphenylacetaldehyde and the diastereomer of the starting material were formed. (*Meso*-hydrobenzene sulfite 2b has two geometrical isomers because of the tetrahedral geometry assumed by the sulfur atom. Two isomers differing in the orientation of the exocyclic oxygen atom are isolable at room temperature. The major and minor isomers are distinguishable by ^1H nuclear magnetic resonance spectroscopy [3]. For convenience the major isomer was used in the present study.) During photolysis a "photostationary" diastereomeric mixture of *d,l* and *meso* forms in about a 1:4 ratio was produced from both 1b and 2b. In each system, NTMB was recovered in greater than 95% yield after complete conversion of the substrate. Irradiation of the substrates at 340 nm in the absence of NTMB resulted in no detectable reaction.

3. Discussion

The direct photolysis of 1 and 2 is reported to lead to the following products:





We propose a reversible electron transfer mechanism (Fig. 1) to rationalize the NTMB-photosensitized decompositions of 1 and 2. In our systems the singlet state of NTMB is formed exclusively by 340 nm excitation. The lifetime of NTMB has been determined [4] to be about 10×10^{-9} s and ϕ_f to be 0.30, giving a fluorescence rate of $3.0 \times 10^7 \text{ s}^{-1}$. ϕ_{ST} was determined to be 0.63, yielding a singlet-triplet intersystem crossing rate of $6.7 \times 10^7 \text{ s}^{-1}$ [5].

Each of the substrates was found to quench (at appropriate concentrations) both $^1\text{NTMB}^*$ and $^3\text{NTMB}^*$. Each of the substrates quenched NTMB fluorescence with a rate constant of $(8 - 9) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Thus, at the concentrations of substrates employed (0.01 M), the rate of quenching of NTMB was about $8.5 \times 10^7 \text{ s}^{-1}$, a value comparable with the rates of fluorescence and intersystem crossing of NTMB.

The triplet quenching rate constants were determined by laser flash absorption spectroscopy via monitoring the decay of the triplet-triplet absorption of $^3\text{NTMB}^*$ (at 510 nm) [5] in the presence of varying amounts of substrate. Conventional plots of reciprocal lifetime of $^3\text{NTMB}^*$ versus concentration were linear and allowed evaluation of the quenching constants of $(9.6 \pm 1.9) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for 1a and between $(2 - 3) \times 10^6 \text{ mol}^{-1} \text{ s}^{-1}$ for 2a and 2b.

The singlet energies E_s of the substrates were estimated from the onset of their longest wavelength absorption. Since the E_s of NTMB (from fluorescence) was found to be 83 kcal mol^{-1} , conventional singlet energy transfer from NTMB is excluded as a photosensitization mechanism. Conventional triplet-triplet energy transfer from NTMB can also be discounted, since both acetophenone ($E_t = 74 \text{ kcal mol}^{-1}$) and benzophenone ($E_t = 69 \text{ kcal mol}^{-1}$)

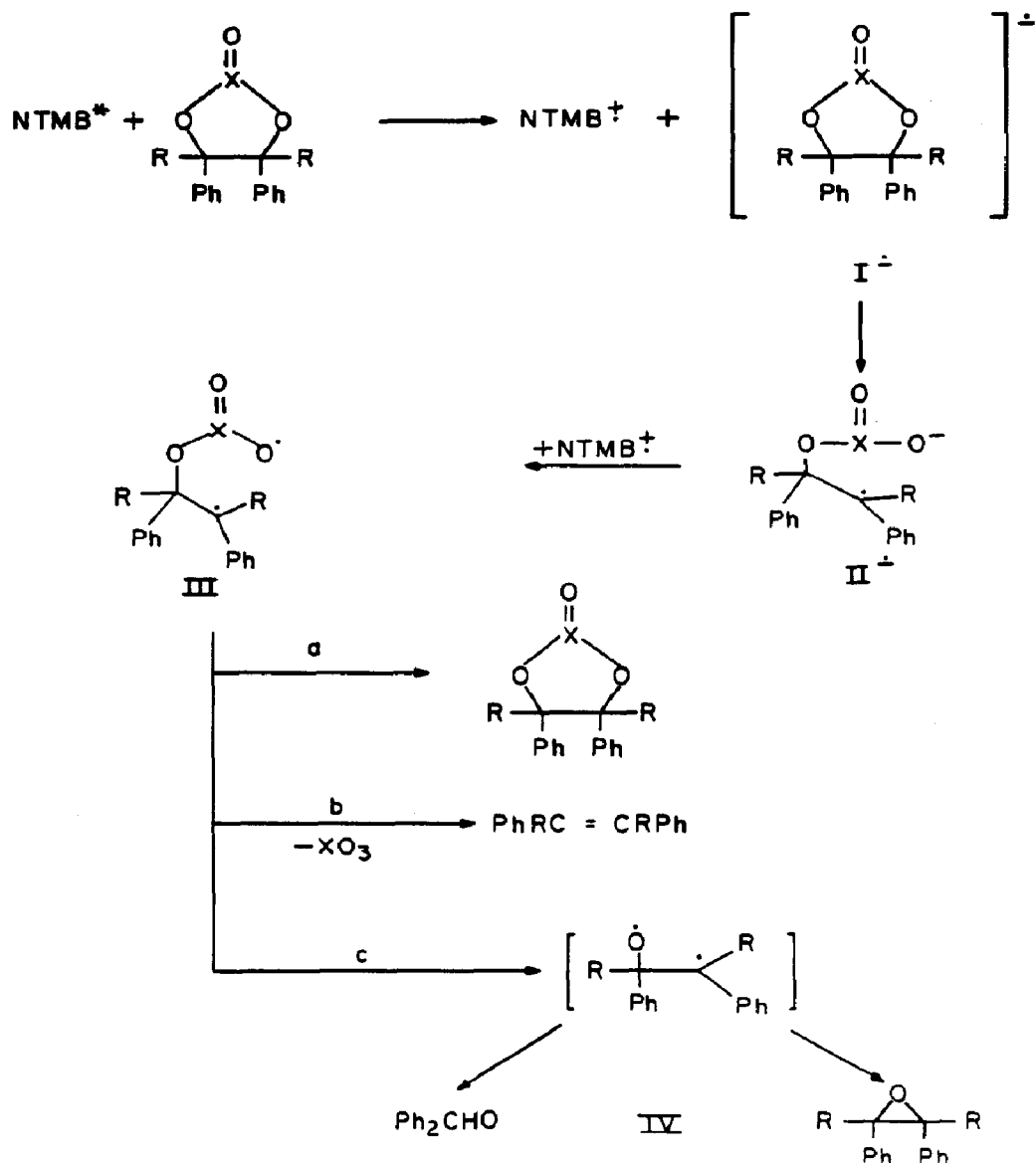


Fig. 1.

[6] are ineffective as sensitizers for the reactions, whereas the lower energy triplet NTMB ($E_t = 63 \text{ kcal mol}^{-1}$) [5] is effective.

The data require that a mechanism other than conventional electronic energy transfer be responsible for the photosensitized reactions of 1 and 2, and this is an important factor in our proposal of the electron transfer mechanism of Fig. 1. Further, indirect evidence is available from studies in which the ring opening of aryloxiranes has been photosensitized by electron acceptor sensitizers, such as 1,4-dicyanonaphthalene (DCN). An electron transfer from the ground state oxirane to the excited singlet state of DCN was proposed as a key step in the photosensitization mechanism [7]. Finally,

the proposal that the reaction proceeds via electron transfer from the excited states of NTMB is in accord with conclusions we have drawn concerning the NTMB photosensitized rearrangement of aryloxiranes and decomposition of dibenzylsulfone [4].

It is proposed that the mechanism involves electron transfer from the NTMB to 1 or 2. Since 2,3-diphenyloxirane does not quench the excited states of NTMB [8], we suggest that the electron transfer is from NTMB to the sulfite (or carbonate) ring of 1 (or 2), *i.e.* in Fig. 1 to form a radical anion $I'^{\cdot-}$. Cleavage of the latter is expected because of the stabilities of both the radical and the anion which are produced in the ring-opened radical ion $II'^{\cdot-}$.

Back electron transfer to $NTMB'^{+}$, which must occur at some point along the reaction pathway, is postulated to occur from $II'^{\cdot-}$, in Fig. 1, to produce the ring-opened diradical III. The diradical is proposed to lead to the observed products as shown in paths a, b and c. Cyclization of III (path a) may occur with loss of initial stereospecificity if III corresponds to a triplet diradical since, in this case, C—C bond rotation is competitive with intersystem crossing. The favored formation of the *meso* isomer on ring closure may be due to steric effects or to different rates of the electron transfer processes for the two isomers. The oxirane products are expected as a result of loss of CO_2 or SO_2 from the diradicals III (path c). The diphenylacetaldehyde rearrangement products are viewed as resulting from 1,2-diphenyl migration in diradical III or IV. The formation of tetraphenylethylene (path b) from 1a (and 2a) involves formal loss of SO_3 (or CO_3). The details of the mechanism of this path are not known.

4. Conclusion

The photosensitized fragmentation of cyclic sulfites and cyclic carbonates follows a reversible electron transfer mechanism analogous to that proposed for photosensitized fragmentation of sulfones and esters [4]. It may be concluded from the proposed mechanism that, since no carbene products are observed by diradical cleavage (Fig. 1, path c), the formation of carbenes on direct photolysis of oxiranes results from C—C bond rather than C—O bond cleavage.

5. Experimental details

5.1. Materials

NTMB (Aldrich) was used as supplied. Purification by recrystallization from ethanol was found to have no effect on the results. The preparation of the cyclic aryl pinacol sulfites 1 and carbonates 2 has been reported [1, 2]. Spectrograde solvents were used in all cases.

5.2. Photolysis

A solution of substrate (0.01 M) and NTMB (0.005 M) in acetonitrile was deoxygenated by argon purging and was irradiated at 340 nm using a 1000 W Xe-Hg lamp source with a high intensity monochromator. Analysis was performed by high pressure liquid chromatography on a Du Pont instrument using a reverse phase C18 column and a 1:9 (by volume) mixture of water and methanol as eluting solvent and by vapor phase chromatography on a Varian Aerograph 3700 with a 3% OV-17 column (6 ft \times 1/8 in). All products were identified on the basis of known retention times of authentic compounds and confirmed by vapor phase chromatography combined with mass spectrometry analysis.

5.3. Determination of quenching constants

The photophysics of NTMB has been reported [4]. The fluorescence quenching constants were determined by the measurement of the fluorescence intensity in the presence of varying amounts of substrate. Fluorescence spectra were recorded using a Hitachi-Perkin-Elmer MPF-3L spectrometer. The quenching constants for the NTMB triplet state were determined by laser flash photolysis using a Lambda Physik EMG 101 laser (308 nm; 15 ns) in a manner which has previously been described [9].

Acknowledgments

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