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PHOTOSENSITIZED CARBON-OXYGEN BOND CLEAVAGE REACTION OF EPOXIDES BY 2,4,6-TRIPHENYLPYRYLIUM TETRAFLUOROBORATE SALT[1)]

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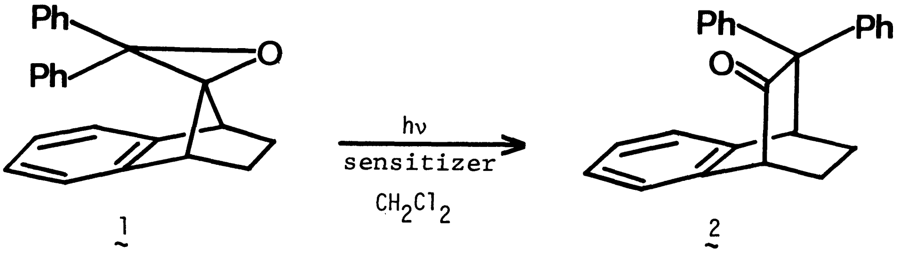
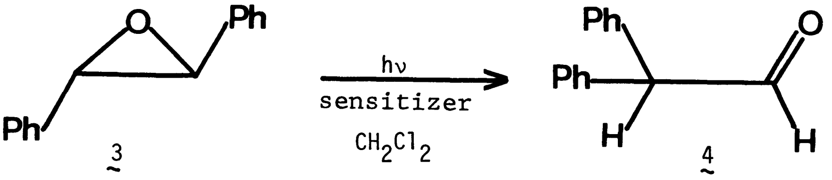
The carbon-oxygen bond cleavage of epoxides, (1) and (3), was photochemically sensitized by 2,4,6-triphenylpyrylium tetrafluoroborate in methylene chloride to give carbonyl compounds, (2) and (4), with high efficiency (Φ>1) respectively. The reaction efficiency was strongly dependent on solvents and counter ions of the sensitizer.

Although the acid-catalyzed or photochemical ring-opening reactions of epoxides have been well investigated, recent attention has centered on the reactivity of the cation radical of epoxides. Albini and Arnold[2)] reported that the carbon-carbon bond cleavage of cis- and trans-stilbene oxides. The proposed mechanism involves an electron transfer process. However, more recently Simonet and his co-workers reported that the electrochemically generated cation radicals of epoxides resulted in the exclusive carbon-oxygen bond cleavage to give rearranged ketones in methylene chloride or dry acetonitrile.[3)] Both of the carbon-carbon and carbon-oxygen bond cleavages of epoxides in the anodic-oxidation reactions were observed by Miller et al.[4)] Thus the results from photosensitized and electrochemical reactions are conflicting each other. We wish to report here that a new type of photochemical reaction of epoxides effectively results in the exclusive carbon-oxygen bond cleavage to give ketones.

When a methylene chloride solution of epoxide (1) (1.93×10^{-2} mol dm^{-3}) and 2,4,6-triphenylpyrylium tetrafluoroborate (1.55×10^{-3} mol dm^{-3}) was irradiated with a 300 W Xenon lamp through Corning 3-74 filter (>400 nm) for 15 min, the ketone (2) was quantitatively formed. The reaction showed the following interesting aspects: i) the quantum yield was over unity (Φ= 22.3 at [1]= 2.32×10^{-2} mol dm^{-3} and [sensitizer]= 5.09×10^{-4} mol dm^{-3}); ii) 2,4,6-triphenylpyrylium tetrafluoroborate or tri-p-methoxyphenylmethyl tetrafluoroborate was effective as a sensitizer, but 1 was recovered quantitatively when the corresponding perchlorate or chloride salt was used, suggesting that tetrafluoroborate anion seems to be essential for the reaction;[5)] iii) the reaction occurred in methylene chloride, chloroform, or ethylbromide, but did not occur in acetonitrile, acetone, methanol, ethylacetate, benzene, or carbon tetrachloride; iv) the reaction was effectively quenched by a small amount of diazabicyclo[2.2.2]octane (1.67×10^{-3} mol dm^{-3}) and virtually no ketone was formed; v) the reaction was relatively



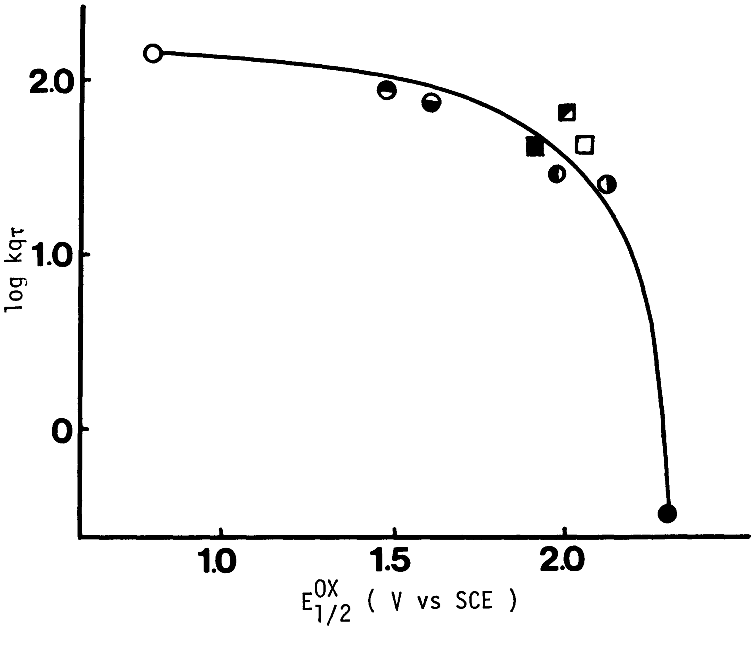


insensitive to the presence of oxygen, since degassing the sample did not affect the reaction efficiency (Φ= 23.0, at [1]= 1.16 X 10^{-2} mol dm^{-3} and [sensitizer]= 5.09 X 10^{-4} mol dm^{-3}); vi) a similar reaction was observed for trans-stilbene oxide (3) (Φ= 2.4 at [3]= 2.55 X 10^{-2} mol dm^{-3} and [sensitizer]= 3.79 X 10^{-3} mol dm^{-3}), but no reaction for 1,1,2,2-tetraphenylethylene oxide. Among the above observations outstanding is high selectivity toward the solvents and the sensitizers. The solvent effect can not be explained in terms of heavy atom effect because this reaction did not occur in carbon tetrachloride. Although the pyrylium salt is well known as a sensitizer which causes an electron transfer from substrates,6) an electron-transfer mechanism simply involving the transformation of $1^{+\cdot}$ to $2^{+\cdot}$ can not explain the above observations. On the other hand the results i), ii), and iv) may remind us of the generation of acid species such as BF_3 and HBF_4 during the photolysis. In fact, both BF_3 and $HBF_4$7) catalyzed the above reaction and gave 2 at [BF_3-Et_2O]= 5 X 10^{-3} mol dm^{-3} or [HBF_4]= 4 X 10^{-3} mol dm^{-3} after treating for 15 min at room temperature. Furthermore the fact that 1,1,2,2-tetraphenylethylene oxide was at least 10 times less reactive toward BF_3 than 1 or 3 may support an acid-catalyzed reaction mechanism.

However, the following findings appear to conflict with an acid-catalyzed mechanism: i) the reactivity of 1 was only 1.5 times greater than that of 3 in BF_3 catalyzed dark reaction, while the quantum yield of 1 was about 10 times greater than that of 3 in the photosensitized reaction; ii) after irradiation of a methylene chloride solution of 1 and 2,4,6-triphenylpyrylium tetrafluoroborate for 15 min which had led to the quantitative conversion of 1 to 2, 1 was newly added into the reaction mixture, but no change of the 1 occurred in the dark; iii) although the acid-catalyzed dark reaction was not affected by a quencher, 1,2,4,5-tetramethoxybenzene, the photosensitized ring-opening reaction was completely quenched by a small amount of the quencher (1.01×10^{-3} mol dm^{-3}). At this concentration, only less than 15% ($kq\tau$= 138 $mol^{-1}dm^3$) of the excited singlet of the sensitizer was quenched.

To rationalize the above observations in terms of an acid-generation mechanism, it seems necessary to assume that at least one of the processes in which the acids are produced should be quenched by 1,2,4,5-tetramethoxybenzene ($E^{ox}_{1/2}$= + 0.81 V vs SCE),[8] and that the acids should disappear in the dark after irradiation.

In order to seek the clue for the primary process of the photoreaction, the fluorescence quenching of the sensitizer was examined in methylene chloride. The epoxides quenched the fluorescence in high efficiencies ($kq\tau$= 36 $mol^{-1}dm^3$ for 1 and 39 $mol^{-1}dm^3$ for 3), while neither methylene chloride nor BF_4 anion (tetra-n-butylammonium tetrafluoroborate) appreciably quenched the fluorescence. The relation between the oxidation potentials ($E^{ox}_{1/2}$ V vs SCE)[8,9] of the quenchers and the values of log $kq\tau$ was shown in the Figure. The quenching most likely arises from electron transfer,[10,11,12] since the efficiency of the quenching falled on the curve plotted toward the oxidation potentials of several electron donors.



Figure

Plots of fluorescence quenching efficiencies (log $kq\tau$) against oxidation potentials ($E^{ox}_{1/2}$ V vs SCE) of quenchers. ● benzene, ◑ coumarin, ◐ toluene, ◒ 1,2,4,5-tetramethylbenzene, ◓ 1,3,5-trimethoxybenzene, ○ 1,2,4,5-tetramethoxybenzene, □ epoxide (1), ■ epoxide (3), ◪ 1,1,2,2-tetraphenylethylene oxide.

Thus, the reaction appears to have a dual character involving an acid generation under the illuminated conditions, and an electron transfer as a primary process. To solve the discrepancy, one of the possible mechanisms may be such that the radical ions formed from the primary electron transfer process may induce the generation of acids under the conditions. High selectivity toward the solvents and the counter ions of the sensitizer may participate in the latter process.

However, in spite of considerable efforts to clarify the detail of the reaction mechanism for this particular example, some important questions still remain unsolved, i.e. why methylene chloride is effective and how acid species, if the acid-generation mechanism under irradiated conditions operates, are generated. The answer has to be awaited the full potential of this and the related studies.

References

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12) An additionally interesting and complicated result was provided by the observation that the quantum yield of the photosensitized reaction of 1 ($E^{ox}_{1/2}$= + 2.07 V vs SCE, $k_q\tau$= 36 $mol^{-1}dm^3$) decreased to less than 0.4 on adding 3 ($E^{ox}_{1/2}$= + 1.92 V vs SCE, $k_q\tau$= 39 $mol^{-1}dm^3$). The quantum yield for 3 was 1.6 under this condition.

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