

The Formation of Ozonides by Electron Transfer Induced Photo-oxidation of Small-ring Cycloalkenes¹

Gary P. Kirschenheuter and Gary W. Griffin*

Department of Chemistry, University of New Orleans, Lake Front, New Orleans, Louisiana 70148, U.S.A.

Several polymethyl-1,2-diphenylcyclobutenes have been subjected to photo-oxidation in acetonitrile in the presence of 9,10-dicyanoanthracene and it is possible to isolate the corresponding ozonides, in moderate yields (ca. 13%), apparently formed from oxirans produced in a primary step; 1,4-diketones are not generated from the ozonides under the reaction conditions although they are formed as reaction products by what must be an alternative mechanism.

In view of the recent report by Schaap and co-workers² on the 9,10-dicyanoanthracene (DCA) sensitized oxygenation of tetraphenyloxiran (1) to give the ozonide (2), we report the results of recent related experiments conducted in our laboratories.† During the course of our continuing investigation of the sensitized photo-oxidation of strained stilbenes such as the cyclopropenes (3a–d) and cyclobutenes (4a–c)³ we subjected 3,3,4,4-tetramethyl-1,2-diphenylcyclobutene (4a) to DCA sensitized photo-oxidation. Compelling evidence showed that the oxidation affords the stable ozonide (5a).⁴ The conversion of (4a) into the ozonide (5a) constitutes the first report, to our knowledge, of the formation of such a product upon sensitized photo-oxidation of an alkene.

When an oxygen saturated acetonitrile solution of (4a) (10^{-2} M) containing DCA (10^{-4} M) is irradiated at 400–430

nm‡ for 1.0 h the following products are obtained: (4a) (38.2%), diketone (6) (13%), oxiran (7) (6.7%), ozonide (5a) (13.1%), benzil (10.5%), and a mixture of benzoic anhydride and as yet unidentified products (18.5%).

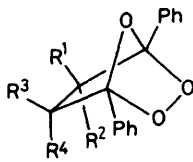
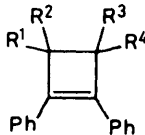
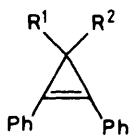
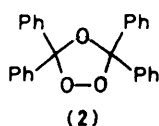
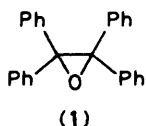
The structure of the diketone (6) was established by comparison with an authentic sample⁴ while the oxiran (7), a known compound, was identified by independent synthesis *via* peracid oxidation of (4a).⁵ A sample of the ozonide (5a) was obtained independently by ozonolysis of (4a) according to published procedures.⁴ Comparison of the ¹H n.m.r., ¹³C n.m.r., i.r., and mass spectral data of the ozonolysis product with those of the adduct obtained by photo-oxidation of (4a) confirms the identity of (5a). No depression in melting points was observed in a mixed melting point determination.

Once the structure of the ozonide (5a) was established, it was of interest to obtain information regarding the origin of this unexpected product. That photogenerated ozone was implicated in the oxidation of (4a) was excluded by a control experiment.§ The isolation of small quantities of the oxiran (7) upon oxidation of (4a) and consideration of Schaap's² report of ozonide formation from tetraphenyloxiran (1) led us to speculate that the oxiran (7) is formed in the primary photo-oxidation step, but is efficiently oxidized to the ozonide (5a) under the reaction conditions.

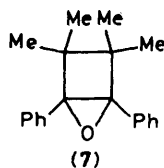
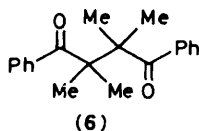
To test the plausibility of this mechanistic scheme a sample of oxiran (7) was prepared and subjected to DCA sensitized photo-oxidation. Under the conditions employed, (7) is converted into ozonide (5a) in 94% yield thus demonstrating the feasibility of the proposed process.

It is widely accepted that DCA sensitized photo-oxygenations involve the formation of superoxide radical anion which subsequently reacts with the radical cation of an alkene substrate.⁶ It is of interest in the context of this work to establish whether or not the intermediacy of superoxide radical anion is implicated in the formation of the oxiran (7).

Foote and co-workers⁷ observe that the course of the DCA sensitized photo-oxidation of *trans*-stilbene is modified upon addition of benzoquinone (BQ). They attribute the change in reaction course to efficient interception of superoxide radical anion by BQ. When the photo-oxidation of (4a) is conducted in the presence of BQ at the concentration level suggested (2×10^{-3} M), no significant changes in product distribution and relative conversion levels were observed after 2 h irradiation. These results suggest that the photo-oxidation of (4a) sensitized by DCA does not proceed *via* a mechanism



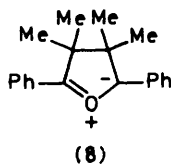
- (3)a, R¹=Ph, R²=H
 b, R¹=Ph, R²=Me
 c, R¹=R²=Ph
 d, R¹=R²=Me
- (4)a, R¹=R²=R³=R⁴=Me
 b, R¹=R²=R³=Me, R⁴=H
 c, R¹=R²=Me, R³=R⁴=H
- (5)a, R¹=R²=R³=R⁴=Me
 b, R¹=R²=R³=Me, R⁴=H
 c, R¹=R²=R³=Me, R⁴=H



† Satisfactory elemental analyses for carbon, hydrogen, and nitrogen were obtained for all new compounds. Physical constants: (5a) m.p. 150–151 °C, (6) m.p. 113–114 °C, and (7) m.p. 117–118 °C.

‡ Irradiations were conducted in a Pyrex immersion type vessel into which oxygen was continuously bubbled. The light source employed consisted of a 500 W Hanovia medium pressure mercury vapour lamp in conjunction with an aqueous filter solution composed of 27 g CuSO₄, 30 g NaNO₂, and 50 ml NH₄OH diluted to 1 l.

§ A 10^{-4} M solution of DCA in MeCN was irradiated as oxygen was continuously passed through the solution. The escaping oxygen stream potentially containing the photogenerated ozone was conducted to a dark reaction zone consisting of a flask containing (4a) dissolved in CH₂Cl₂ at –78 °C surrounded by an opaque shield. No ozonide formation was detected after 4 h of irradiation. Similarly, no ozonide was formed in a second control experiment in which biphenyl was added to the DCA solution to promote the formation of superoxide radical anion.²



involving superoxide radical anion as a reactive intermediate. Presumably, the oxiran (7) is formed initially and subsequently oxidized to the ozonide (5a) in the absence of superoxide radical anion, conceivably *via* the intermediate carbonyl ylide (8). This result is at variance with the mechanism advanced by Schaap and associates for the photo-oxidation of tetraphenyl-oxiran (1)² to the ozonide (2) in which the radical cation of (1) is proposed to react directly with superoxide radical anion to yield the ozonide (2).¶

An isomeric pair of ozonides (5b) and (5c) is likewise obtained upon photosensitized oxidation of trimethylcyclobutene (4b) in the presence of DCA. These isomers were differentiated by their ¹H n.m.r. spectra which exhibit low and high field methyl doublets assigned to the *endo*- and *exo*-4-methyl substituents, respectively.** It remains to be established whether or not ozonides are also intermediates in the photo-

¶ *Added in proof.* Additional information pertaining to the mechanism proposed for ozonide formation from the cyclobutane (4a) has been obtained in collaboration with Professor A. P. Schaap, and co-workers, and will be the subject of a future joint publication.

** ¹H n.m.r.: δ(CDCl₃, 90 MHz), (5b): 0.875 (s, 3H), 1.15 (d, 3H, *J* 7 Hz), 1.22 (s, 3H), 2.30 (d, 1H, *J* 7 Hz), and 7.25–7.57 (m, 10 ArH); (5c): 0.69 (d, 3H, *J* 7.6 Hz), 0.72 (s, 3H), 1.45 (s, 3H), 2.65 (q, 1H, *J* 7.6 Hz), and 7.23–7.52 (m, 10 ArH); ¹³C n.m.r.: (CDCl₃), (5b): 131.0 (s), 130.7 (s), 129.8 (d), 129.1 (d), 128.5 (d), 128.0 (d), 126.9 (d), 126.2 (d), 115.5 (s), 113.0 (s), 50.3 (s), 45.9 (d), 29.0 (q), 17.8 (q), and 9.8 p.p.m. (q); *m/z*: (5b): 280, 264, 249, 255 (metastable), 226, 198, 174, 159, 148, 131, 122, 105 (base), 77, and 70; ¹³C n.m.r. and mass spectral data for (5c) were comparable.

oxidative conversion of cyclopropenes (3a–d) into their respective diketones³ which appears unlikely in view of the facile rearrangement of oxabicyclobutanes to α,β-unsaturated ketones.^{3c}

We note with interest that the spectrum of products obtained upon DCA sensitized photo-oxidation of stilbene and tolan parallel those obtained upon decomposition of their respective ozonides.^{6,8,9}

This work was supported in part by the National Science Foundation and the Cancer Association of Greater New Orleans (Summer Cancer Student Research Grant, June, 1982 to August, 1982).

Received, 3rd February 1983; Com. 168

References

- 1 Presented in part at the 15th Mardi Gras Symposium in Organic Chemistry, Louisiana State University, Chemistry Department, Baton Rouge, La., February 14, 1983; taken in part from the Doctoral Dissertation of G. Kirschenheuter, University of New Orleans, New Orleans, La., 1983.
- 2 A. P. Schaap, L. Lopez, and S. D. Gagnon, *J. Am. Chem. Soc.*, submitted for publication; presented in part at the IXth IUPAC Symposium on Photochemistry, Pau, France, July 25–30, 1982, Abst. ST 15.
- 3 Our preliminary studies published in this area include (a) I. R. Politzer and G. W. Griffin, *Tetrahedron Lett.*, 1973, 4775; (b) G. W. Griffin, I. R. Politzer, K. Ishikawa, N. J. Turro, and M.-F. Chow, *ibid.*, 1977, 1287; (c) C. Vaz, G. W. Griffin, S. Christensen, and D. Lankin, *Heterocycles*, 1981, **15**, 1643.
- 4 W. M. Williams and W. R. Dolbier, Jr., *J. Am. Chem. Soc.*, 1972, **94**, 3955.
- 5 D. R. Arnold and L. A. Karnischky, *J. Am. Chem. Soc.*, 1970, **92**, 1404.
- 6 J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 6083.
- 7 L. E. Manring, M. K. Kramer, and C. S. Foote, results communicated prior to publication.
- 8 S. Jackson and L. A. Hull, *J. Org. Chem.*, 1976, **41**, 3340.
- 9 S. L. Mattes and S. Farid, *J. Chem. Soc., Chem. Commun.*, 1980, 457.