

Rick C. White* and Sha Ma

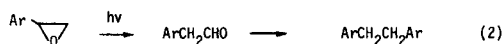
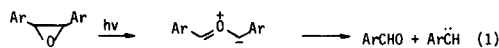
Department of Chemistry, Sam Houston State University,
Huntsville, TX 77341

Received February 19, 1987

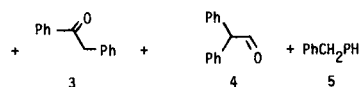
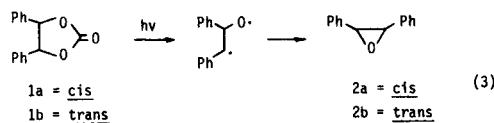
The photolysis of the mono substituted cyclic carbonate ester 4-phenyl-1,3-dioxolan-2-one has been studied. The direct irradiation results in loss of carbon dioxide with the formation of the corresponding oxirane, styrene oxide as well as phenylacetaldehyde and bibenzyl. Photolysis in methanol produces the same compounds in addition to phenethyl alcohol and 2-methoxy-2-phenylethanol. Triplet sensitized photolyses resulted in the products derived entirely from benzyl radicals with none of the oxirane being detected.

J. Heterocyclic Chem., **24**, 1203 (1987).

Some time ago [1], it was found that vicinal diaryl oxiranes produced carbonyl ylids upon irradiation which underwent further reaction to produce an aryl aldehyde and an aryl substituted carbene. The latter was characterized by additions to double bonds [2], insertion reactions [3], and by trapping with methanol [4]. In contrast, mono-aryl oxiranes gave only products derived from free radicals [5]. These reactions are shown in equations 1 and 2.

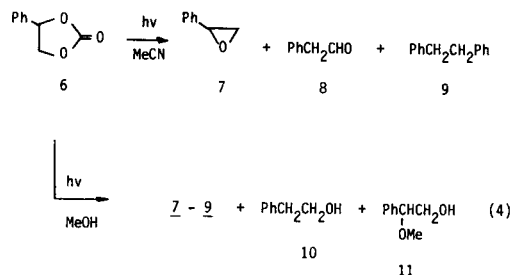


Although the irradiation of vicinal diaryl cyclic carbonate esters **1a** and **1b** have been reported to give carbenes [6], we have found that the major photochemical pathway is formation of a 1,3-diradical which undergoes ring closure to produce epoxides **2a** and **2b**, H migration to provide ketone **3** and aryl migration to afford aldehyde **4** and diphenylmethane [7].

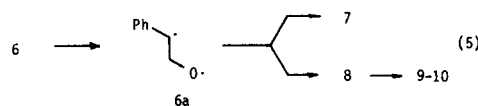


In view of the differences in reactivity between mono-aryl and vicinal diaryl oxiranes, we undertook a study of the photolysis of the monoaryl substituted cyclic carbonate ester, 4-phenyl-1,3-dioxolan-2-one (**6**) to compare its photochemistry with that of **1a,b**.

We found that the direct irradiation of a 0.1 M solution of **6** in acetonitrile at 254 nm for 2.5 hours afforded styrene oxide (**7**), phenylacetaldehyde (**8**) and bibenzyl (**9**) in addition to unaltered starting material. When the same reaction was carried out in methanol, products **7-9** were formed along with phenethyl alcohol (**10**) and 2-methoxy-2-phenylethanol (**11**). These are shown in equation 4.



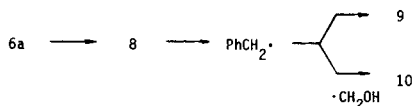
This seems to follow the case of cyclic carbonate esters **1a** and **1b** in which extrusion of carbon dioxide occurs to produce a 1,3-diradical which either undergoes ring closure to produce **7** or H-migration to form **8**. Subsequent decarbonylation of **8** produces benzyl radicals which either dimerize to form **9** or react with solvent to form **10**. An alternative mechanism would consist of the concerted formation of **7** followed by secondary photoproducts to produce **8-11**. However, analysis of the reaction mixture by hplc through the first twelve minutes showed that **8** was indeed a primary photoproduct consistent with the formation of diradical intermediate **6a**.



We observed that although **10** and **11** have been reported as products of the photolysis of **7** in methanol [8,9], only **10** was a primary photoproduct of **6** while **11** seems to be the result of an acid catalyzed ring opening of

7 [9].

The photolysis of **6** under sensitized conditions (0.1 *M* in 4 *M* acetone/acetonitrile, 300 nm) produced **9** as the only major photoproduct with none of the epoxide **7** being detected. When the same reaction was carried out in 4 *M* acetone/methanol, phenethyl alcohol was the only major photoproduct with only a trace of **9** being formed. Thus, in the triplet state, intermediate **6a** does not undergo ring closure but rather rearranges to **8** and then decarbonylates to benzyl radicals which either dimerize or react with solvent radicals.



The fact that we did not see an appreciable amount of **8** in the sensitized reactions is not surprising. The triplet state of **8** reacts fast enough for complete consumption after 18 hours. We found that the acetone sensitized irradiation of **8** in acetonitrile to form **9** was 80% complete in only four hours.

Thus, we find that the photoextrusion of carbon dioxide from cyclic carbonate esters to form epoxides has been expanded to include the monoaryl derivative **6** and that epoxide formation is a singlet state process. The results of these irradiations are shown in Table 1

Table 1

Photolysis of 4-Phenyl-1,3-dioxolan-2-one [a]

Exp	Conditions	% reaction	7	8	9	10	11
1	direct (acetonitrile)	65	16%	30%	17%	—	—
2	direct (methanol)	70	21%	15%	10%	8%	5%
3	sen. (acetonitrile)	56	—	—	67%	—	—
4	sen. (methanol)	58	—	—	tr	52%	—

[a] Direct irradiations = 2.5 hours; sen. irradiations = 18 hours. Yields are based on amount of starting material consumed. For details, see Experimental.

EXPERIMENTAL

All nmr spectra were obtained with a Varian EM 360L nuclear magnetic resonance spectrometer. Infrared spectra were recorded using a PE 559B spectrometer. Analyses of reaction mixtures by gc/ms were carried out using a Hewlett Packard 5992B gas chromatograph/mass spectrometer equipped with a 3' x 1/8" glass column of 2% OV-101. The gc parameters were set at: injector port = 120°; initial column temperature = 100°; rise time = 6°/minute; final column temperature = 200°; carrier gas = helium. Retention times and mass spectra were compared to those of authentic samples. The hplc measurements were carried out with a Tracor 990 liquid chromatograph with a reversed phase C-18 column using 60/40 methanol/water as eluent. Toluene was used as an internal standard.

Styrene oxide, phenylacetaldehyde, bibenzyl and phenethyl alcohol were commercially available (Aldrich). A sample of 2-methoxy-2-phenylethanol was prepared from styrene oxide as described by Winstein [10].

Photochemical reactions were carried out using a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co.) equipped with either 8 RPR-2537 lamps or 4 RPR-3000 lamps. The reaction mixtures were placed in quartz tubes fitted with a rubber septum and sparged with

deoxygenated nitrogen for 30 minutes prior to irradiation.

4-Phenyl-1,3-dioxolan-2-one (6).

Styrene glycol (1.38 g, 10 mmoles) and 1,1'-carbonyldiimidazole (1.62 g, 10 mmoles) were dissolved in 50 ml of benzene in a 100 ml round bottom flask and heated at reflux temperature for 3 hours. The solution was cooled, washed with water (2 x 25 ml), dried (sodium sulfate), and the benzene removed to give an oil. The oil was crystallized from benzene/hexane to provide 1.05 g (64%) of **6**, mp 54-55°, lit [11] 53-55°, whose nmr spectrum was identical to that reported [12].

Photolysis of 4-Phenyl-1,3-dioxolan-2-one (6).

(a) Direct Photolysis in Acetonitrile.

A sample of **6** (0.25 g 1.5 mmoles) was dissolved in purified acetonitrile (15 ml) and placed in a quartz phototube. After sparging with nitrogen for 30 minutes, the sample was irradiated for 2.5 hours. The solvent was removed and the mixture analyzed by nmr. The nmr spectrum revealed signals for unaltered **6** [12] and for products **7-9**. The amounts of each could be calculated by adding toluene as an internal standard.

(b) Direct Photolysis in Methanol.

The same procedure in (a) was carried out using methanol as the solvent. Both nmr analysis and gc/ms analysis of the photolysate revealed the presence of **10** and **11** in addition to products **7-9**.

(c) Sensitized Photolysis in Acetonitrile.

A sample of **6** (0.25 g, 1.5 mmoles) was dissolved in 15 ml of 4 *M* acetone in acetonitrile, placed in a quartz tube and sparged for 30 minutes prior to photolysis. Analysis of the photolysate after 18 hours of irradiation by both nmr and gc/ms showed bibenzyl as the only major photoproduct.

(d) Sensitized Photolysis in Methanol.

The same procedure in (c) was followed using 4 *M* acetone in methanol as the solvent. Analysis of the photolysate by nmr and gc/ms showed **10** as the only major photoproduct and a trace of **9**.

Analysis of Photolyses at Short Reaction Times.

To each of four quartz tubes (13 x 100 mm) were placed 5.0 ml samples of a 0.06 *M* solution of **6** in either acetonitrile or methanol. These were sparged with nitrogen and placed in a Rayonet Reactor. The lamps were turned on and the tubes removed at 3, 6, 9, and 12 minutes and then analyzed by hplc using toluene as the internal standard.

Acknowledgement.

We are grateful to the donors of the Petroleum Research Fund administered by the American Chemical Society for the generous support of this work.

REFERENCES AND NOTES

- [1] R. S. Becker, R. O. Bost, J. Kolc, N. R. Bertoniere, R. L. Smith, and G. W. Griffin, *J. Am. Chem. Soc.*, **92**, 1302 (1970).
- [2] H. Kristinsson and G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, **4**, 868 (1965).
- [3] H. Dietrich and G. W. Griffin, *Tetrahedron Letters*, 153 (1968).
- [4] R. L. Smith, A. Manmade and G. W. Griffin, *J. Heterocyclic Chem.*, **6**, 443 (1969).
- [5] H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 1579 (1966).
- [6] G. W. Griffin, R. L. Smith and A. Manmade, *J. Org. Chem.*, **41**, 338 (1976).
- [7] R. C. White and T. Rix, *J. Org. Chem.*, accepted for publication.
- [8] M. Hisaoka and K. Tokumaru, *Chem. Letters*, 351 (1973).
- [9] S. N. Merchant, S. C. Sethi and H. R. Sonawane, *Ind. J. Chem.*, **17B**, 267 (1979).
- [10] S. Winstein and L. L. Ingraham, *J. Am. Chem. Soc.*, **77**, 1738 (1955).
- [11] L. R. Morris and D. J. Hubbard, *J. Org. Chem.*, **27**, 1451 (1962).
- [12] J. Katzhendler, I. Ringel and S. Sarel, *J. Chem. Soc., Perkin Trans. II*, 2019 (1972).