A Convenient Preparative Method of [*m*.*n*.3]Propella-γ-lactones

Tsutomu Fujita, Shoji Watanabe,* Kyoichi Suga, Yoshiki Higuchi, and Tsukasa Sotoguchi

Department of Applied Chemistry, Faculty of Engineering, Chiba University, 1-33, Yayoicho,
Chiba-shi 260, Japan

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The acid-catalyzed reaction of 3-hydroxy acids **2** containing a spiro ring is described. Spiro ketones **1** react with the dianion of carboxylic acids to give 3-hydroxy acids **2**. Treatment of these 3-hydroxy acids **2** with sulfuric acid in boiling benzene takes place readily to yield spiro ring migration to afford [*m*.*n*.3]propella-γ-lactones **3**.

The chemistry of propellanes, particularly, the structure–reactivity relationships, has drawn much attention.[1] Small ring propellanes, such as [*m*.*n*.1]-[2] and [*m*.*n*.2]propellanes[3] have been well investigated. Furthermore, total syntheses of modhephene, a naturally occurring propellane isolated from rayless goldenrod (*Isocoma wrightii*)[4] have been achieved.[5] In these studies, formation of propellane skeletons was usually carried out by photochemical reactions.[6] Propellalactones were prepared from the corresponding propellane ketones by Baeyer-Villiger oxidation.[7] The transformation of propellalactones into other important polycarbocyclic ring systems, dispiro lactones, was also reported.[8] However the preparation of propella-γ-lactones from spiro compounds has not been reported. The present paper will describe the acid-catalyzed reaction of 3-hydroxy acids **2** to afford propella-γ-lactones **3**.

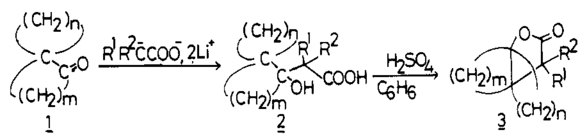
Table I. Preparation of [*m*.*n*.3]Propella-γ-lactones 3 from the Reaction of 2 with Acidic Materials[a]

compd	yield of 2,[b] %	acidic materials	product	yield of 3,[c] %
2a	70	H_2SO_4	**3a**	83
2b	76	H_2SO_4	**3b**	80
2c	93	H_2SO_4	**3c**	98
2c	93	$ZnCl_2$	**3c**	39
2c	93	H_3PO_4	**3c**	93
2c	93	TsOH	**3c**	75
2c	93	P_2O_5	**3c**	95
2c	93	CF_3COOH[d]	**3c**	91
2c	93	$KHSO_4$	**3c**	15
2c	93	Polyphosphoric acid	**3c**	73
2c	93	$SnCl_4 \cdot 5H_2O$	**3c**	63
2d	73	H_2SO_4	**3d**[e]	85
2e	60	H_2SO_4	**3d**[e]	85
2f	65	H_2SO_4	**3e**	87
2g	92	H_2SO_4	**3f**	98
2h	15	H_2SO_4	**3g**	57
2i	90	H_2SO_4	**3h**	65
2j	76	H_2SO_4	**3i**	70

[a] 3-Hydroxy acid **2** (10 mmol), acidic materials (3 mmol), and benzene (300 mL) were refluxed for 8 h. [b] The yields are based on spiroketone used. [c] The yields are based on 3-hydroxy acid used. [d] At 25 °C for 8 h. [e] The same product **3d** was obtained from **2d** and **2e**.

Results and Discussion

We examined the reaction of acetic acid and spiro ketone **1c** using lithium naphthalenide in tetrahydrofuran by our method.[9] However, **2c** was obtained in poor yield. Spiro ketones **1** appear to be less reactive than monocyclic ketones. Hence it is necessary to use excess acetate dianion and longer reaction times in the reaction of **1c** with acetate dianion to obtain **2c** in good yield. We have previously reported the reaction of 3-hydroxy acid **4** (Scheme I), prepared from acetic acid and cyclohexanone, with acidic materials in boiling benzene. From the reaction of **4** with 97% sulfuric acid, the γ-lactone **5** was obtained, and, with *p*-toluenesulfonic acid, the unsaturated carboxylic acid **6** was formed.[9b]



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(1) (a) Ginsburg, D. "Propellanes, Structure and Reactions"; Verlag Chemie: Weinheim/Bergstr., Germany, 1975. (b) Paquette, L. A.; Photis, J. M.; Micheli, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 7899 and references cited therein.

(2) (a) Wiberg, K. B.; Burgmaier, G. J. *Tetrahedron Lett.* **1969**, *10*, 317. (b) Gassman, P. G.; Topp, A.; Keller, J. W. *Ibid.* **1969**, *10*, 1093. (c) Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Am. Chem. Soc.* **1977**, *99*, 2297. (d) Gassmann, P. G.; Armour, E. A. *Tetrahedron Lett.* **1971**, *12*, 1431. (e) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 773. (f) Stohrer, W.-D.; Hoffmann, R. *Ibid.* **1972**, *94*, 779. (g) Parham, W. E.; Egberg, D. C.; Montgomery, W. C. *J. Org. Chem.* **1973**, *38*, 1207. (h) Kunai, A.; Ishii, T.; Odaira, Y. *Chem. Lett.* **1974**, 315. (i) Hamon, D. P. G.; Trenerry, V. C. *J. Am. Chem. Soc.* **1981**, *103*, 4962.

(3) (a) Borden, W. T.; Reich, I. L.; Sharpe, L. A.; Reichi, H. J. *J. Am. Chem. Soc.* **1970**, *92*, 3808. (b) Eaton, P. E.; Nyi, K. *Ibid.* **1971**, *93*, 2786. (c) Paquette, L. A.; Philips, J. C.; Wingard, R. E., Jr. *Ibid.* **1971**, *93*, 4516. (d) Paquette, L. A.; Houser, R. W. *Ibid.* **1971**, *93*, 4522. (e) Peet, N. P.; Cargill, R. L.; Bushey, D. F. *J. Org. Chem.* **1973**, *38*, 1218. (f) Peet, N. P.; Cargill, R. L.; Crawford, J. W. *Ibid.* **1973**, *38*, 1222. (g) Kunai, A.; Yorihiro, K.; Hirata, T.; Odaira, Y. *Tetrahedron* **1973**, *29*, 1679. (h) Eaton, P. E.; Temme, III, G. H. *J. Am. Chem. Soc.* **1973**, *95*, 7508. (i) Kunai, A.; Omori, T.; Kimura, K.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 731. (j) Borden, W. T.; Reich, I. L.; Sharpe, L. A.; Weinberg, R. B.; Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2438. (k) Reference 1(b). (l) Tobe, Y.; Doi, A.; Kimura, K.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 639. (m) Tobe, Y.; Kimura, K.; Odaira, Y. *J. Org. Chem.* **1979**, *44*, 639. (n) Sakai, Y.; Toyotani, S.; Tobe, Y.; Odaira, Y. *Tetrahedron Lett.* **1979**, *20*, 3855. (o) Fukuda, Y.; Negoro, T.; Tobe, Y.; Kimura, K.; Odaira, Y. *J. Org. Chem.* **1979**, *44*, 4557. (p) Sakai, Y.; Tobe, Y.; Odaira, Y. *Chem. Lett.* **1980**, 691. (q) Tobe, Y.; Hayauchi, Y.; Odaira, Y. *J. Org. Chem.* **1980**, *45*, 637. (r) Eaton, P. E.; Jobe, P. G.; Nyi, K. *J. Am. Chem. Soc.* **1980**, *102*, 6636. (s) Tobe, Y.; Terashima, K.; Sakai, Y.; Odaira, Y. *Ibid.* **1981**, *103*, 2307. (t) Tobe, Y.; Hayauchi, Y.; Odaira, Y. *J. Org. Chem.* **1981**, *46*, 5219. (u) Sakai, Y.; Toyotani, S.; Ohtani, M.; Matsumoto, M.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1474. (v) Sakai, Y.; Terashima, K.; Tobe, Y.; Odaira, Y. *Ibid.* **1981**, *54*, 2229. (w) Kakiuchi, K.; Hato, Y.; Tobe, Y.; Odaira, Y. *J. Chem. Soc., Chem. Commun.* **1982**, 6.

(4) Zalkow, L. H.; Harris, III, R. N.; Van Derveer, D. *J. Chem. Soc., Chem. Commun.* **1973**, 420.

(5) (a) Karpf, M.; Dreiding, A. S. *Tetrahedron Lett.* **1980**, *21*, 4569. (b) Smith, III, A. B.; Jerris, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 194. (c) Schostarez, H.; Paquette, L. A. *Ibid.* **1981**, *103*, 722.

(6) As exceptional cases, in the ref 2(a) and 2(b), carbene reactions were used and in 2(c) reductive dehalogenation was used.

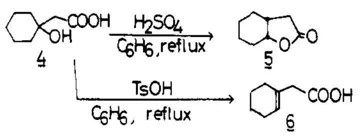
(7) (a) Kakiuchi, K.; Tobe, Y.; Odaira, Y. *J. Org. Chem.* **1980**, *45*, 729. (b) Kakiuchi, K.; Tsugaru, T.; Tobe, Y.; Odaira, Y. *Ibid.* **1981**, *46*, 4204.

(8) (a) Tobe, Y.; Kakiuchi, K.; Kawakami, Y.; Sakai, Y.; Kimura, K.; Odaira, Y. *Chem. Lett.* **1978**, 1027. (b) Kakiuchi, K.; Tobe, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 921.

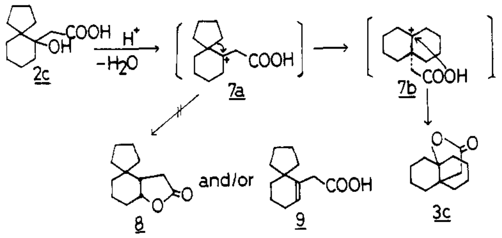
(9) (a) Watanabe, S.; Suga, K.; Fujita, T.; Fujiyoshi, K. *Isr. J. Chem.* **1970**, *8*, 731. (b) Fujita, T.; Suga, K.; Watanabe, S.; Yanagi, R. *J. Appl. Chem. Biotechnol.* **1977**, *27*, 593.

0022-3263/84/1949-1975$01.50/0

Scheme I



Now, we examined the reaction of **2c** with acidic materials. Spiro γ-lactone **8** and/or spiro unsaturated carboxylic acid **9** were not formed, but propella-γ-lactone **3c** was obtained selectively. As Scheme I shows, in the acid-catalyzed reaction of **2c**, carbenium ion **7a** was formed which subsequently gives intermediate **7b** by migration of the spiro bond.[10] The intermediate **7b** leads to propella-γ-lactone **3c**. The reaction of **2c** with several acids was performed and the results are listed in Table I. The reaction has also been extended to other 3-hydroxy acids. As shown in Table I, [*m.n.*3]propella-γ-lactones **3** are obtained in good yield from the reaction of 3-hydroxy acids **2** containing spiro rings with 97% sulfuric acid. These observations indicate that [*m.n.*3] propella-γ-lactones **3** can be easily prepared from spiro ketone **1** by two steps.



Experimental Section

All melting points are uncorrected. The reaction products were analyzed by GLC on a Shimazu Model GC-7A chromatograph using a 3 m × 3 mm glass column of 10% silicone DC 200 on 60–80 mesh Celite 545. Infrared spectra were recorded on a JASCO IR-G spectrometer. ^1H NMR spectra were obtained on a Hitachi R-600 spectrometer with Me_4Si as an internal standard and CCl_4 as a solvent. Mass spectra were measured with a Hitachi RMU-7M spectrometer (for high-resolution mass spectra) at 70 eV. Column chromatography was carried out with silica gel (Wakogel C-200). Microanalyses (C and H) were performed in the Analytical Section of our University.

Spiroketones (**1**) were prepared as previously reported.[11]

3-Hydroxy Acids 2. General Procedure. A mixture of naphthalene (6.4 g, 50 mmol), metallic lithium cuttings (0.7 g, 100 mmol), and diethylamine (7.3 g, 100 mmol) in 100 mL of tetrahydrofuran was agitated at room temperature in an atmosphere of dry nitrogen for 2 h. To the solution was added carboxylic acid[12] (50 mmol) in 50 mL of tetrahydrofuran over a period of 2 h. After 1 h, spiro ketone **1** (25 mmol) in 50 mL of tetrahydrofuran was slowly added and the reaction mixture was stirred for an additional 16 h. 3-Hydroxy acid **2** was separated as reported previously[9a] and purified by recrystallization from hexane or column chromatography.

2a: IR 3400, 1700 cm^{-1}; NMR δ 1.0–2.0 (m, 14 H), 2.50 (s, 2 H), 7.35 (s, 2 H). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.45; H, 9.17.

2b: mp 122–123 °C; IR 3550, 1690 cm^{-1}; NMR δ 1.1–2.0 (m, 16 H), 2.55 (s, 2 H), 6.84 (s, 2 H). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.99; H, 9.48.

2c: mp 78–80 °C; IR 3500, 1700 cm^{-1}; NMR δ 1.0–2.1 (m, 16 H), 2.59 (s, 2 H), 7.58 (s, 2 H). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.72; H, 9.55.

2d: mp 90–91 °C; IR 3500, 1705 cm^{-1}; NMR δ 1.1–1.9 (m, 18 H), 2.59 (s, 2 H), 7.63 (s, 2 H). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.18; H, 9.83.

2e: mp 78–79 °C; IR 3400, 1708 cm^{-1}; NMR δ 1.0–2.0 (m, 18 H), 2.58 (s, 2 H), 7.18 (s, 2 H). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.90; H, 9.71.

2f: IR 3350, 1705 cm^{-1}; NMR δ 0.9–1.8 (m, 20 H), 2.57 (s, 2 H), 7.29 (s, 2 H). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 70.15; H, 10.11.

2g: mp 138–139 °C; IR 3305, 1702 cm^{-1}; NMR δ 1.26 (d, *J* = 7.2 Hz, 3 H), 1.2–1.9 (m, 16 H), 3.01 (q, *J* = 7.2 Hz, 1 H), 7.41 (s, 2 H). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.17; H, 9.83.

2h: mp 184–185 °C; IR 3420, 1700 cm^{-1}; NMR δ 1.31 (s, 6 H), 1.1–1.8 (m, 16 H), 7.36 (s, 2 H). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 69.75; H, 10.14.

2i: mp 131–132 °C; IR 3250, 1695 cm^{-1}; NMR δ 0.97 (t, *J* = 6.5 Hz, 3 H), 1.2–2.1 (m, 18 H), 2.80 (t, *J* = 7.9 Hz, 1 H), 7.75 (s, 2 H). Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.07. Found: C, 70.28; H, 9.94.

2j: mp 123–124.5 °C; IR 3330, 1695 cm^{-1}; NMR δ 0.92 (t, *J* = 6.4 Hz, 3 H), 1.1–2.1 (m, 20 H), 2.77 (t, *J* = 6.4 Hz, 1 H), 7.26 (s, 2 H). Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.92; H, 10.26.

[*m.n.*3]Propella-γ-lactone 3. General Procedure. A mixture of 3-hydroxy acid **2** (10 mmol) and acidic materials (3 mmol) in 300 mL of benzene was refluxed for 8 h. After cooling the mixture to room temperature, 200 mL of water was added. The organic layer was washed with water, 5% sodium carbonate solution, and then dried over anhydrous sodium sulfate. The solvent was removed, and the product was purified.[13]

3a: mp 71–72 °C; IR 1778 cm^{-1}; NMR δ 1.3–2.2 (m, 14 H), 2.52 (q, J_{AB} = 17.2 Hz, 2 H); mass spectrum calcd for $C_{11}H_{16}O_2$, *m/e* 180.1150 (M); found, *m/e* 180.1139 (M^+). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.15; H, 8.82.

3b: IR 1772 cm^{-1}; NMR δ 1.1–2.1 (m, 16 H), 2.51 (q, J_{AB} = 19.1 Hz, 2 H); mass spectrum calcd for $C_{12}H_{18}O_2$, *m/e* 194.1307 (M); found, *m/e* 194.1258 (M^+). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.33; H, 9.22.

3c: mp 73–74 °C; IR 1769 cm^{-1}; NMR δ 1.4–1.9 (m, 16 H), 2.35 (s, 2 H); mass spectrum calcd for $C_{12}H_{18}O_2$, *m/e* 194.1307 (M); found, *m/e* 194.1305 (M^+). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.22; H. 9.30.

3d: IR 1773 cm^{-1}; NMR δ 1.2–1.9 (m, 18 H), 2.38 (s, 2 H); mass spectrum calcd for $C_{13}H_{20}O_2$, *m/e* 208.1463 (M); found, *m/e* 208.1451 (M^+). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.82; H, 9.72.

3e: mp 84–85 °C; IR 1775 cm^{-1}; NMR δ 1.1–1.9 (m, 20 H), 2.39 (s, 2 H); mass spectrum calcd for $C_{14}H_{22}O_2$, *m/e* 222.1620 (M); found, *m/e* 222.1613 (M^+). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.86; H, 9.88.

3f: mp 101–102 °C; IR 1758 cm^{-1}; NMR δ 0.96 (d, *J* = 7.4 Hz, 3 H), 1.1–1.9 (m, 16 H), 2.98 (q, *J* = 7.4 Hz, 1 H); mass spectrum calcd for $C_{13}H_{20}O_2$, *m/e* 208.1463 (M); found, *m/e* 208.1441 (M^+). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.22; H, 9.68.

3g: IR 1765 cm^{-1}; NMR δ 1.15 (s, 6 H), 1.3–1.9 (m, 16 H); mass spectrum calcd for $C_{14}H_{22}O_2$, *m/e* 222.1620 (M); found, *m/e* 222.1609 (M^+). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.77; H, 9.94.

3h: mp 72.5–73.5 °C; IR 1760 cm^{-1}; NMR δ 1.19 (t, *J* = 6.0 Hz, 3 H), 1.4–1.9 (m, 18 H), 2.68 (t, *J* = 6.1 Hz, 1 H); mass spectrum calcd for $C_{14}H_{22}O_2$, *m/e* 222.1620 (M); found, *m/e* 222.1589 (M^+). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.48; H, 10.02.

3i: mp 70–71 °C; IR 1755 cm^{-1}; NMR δ 0.98 (t, *J* = 6.5 Hz, 3 H), 1.2–2.0 (m, 20 H), 2.74 (t, *J* = 6.4 Hz, 1 H); mass spectrum calcd for $C_{15}H_{24}O_2$, *m/e* 236.1776 (M); found, *m/e* 236.1818 (M^+). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.24. Found: C, 76.01; H, 10.29.

Registry No. 1a, 14727-58-3; **1b**, 4728-91-0; **1c**, 13388-94-8;

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[10] The acid-catalyzed dehydration–rearrangement of spiro compounds were reported: Dunham, D. J.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 2075. Takaishi, N.; Inamoto, Y.; Aigami, K. *J. Org. Chem.* **1980**, *45*, 2254.

[11] Krapcho, A. P. *Synthesis* **1974**, 383.

[12] In the case of acetic acid, diethylamine was not used.

[13] The solid products were purified by recrystallization from hexane and the liquid products were purified by column chromatography.

1d, 1781-83-5; **1e**, 73223-32-2; **1f**, 4728-90-9; **2a**, 89789-35-5; **2b**, 89789-36-6; **2c**, 89789-37-7; **2d**, 89789-38-8; **2e**, 89789-39-9; **2f**, 89789-40-2; **2g**, 89789-41-3; **2h**, 89789-42-4; **2i**, 89789-43-5; **2j**, 89789-44-6; **3a**, 89789-45-7; **3b**, 89789-46-8; **3c**, 58564-79-7; **3d**, 89789-47-9; **3e**, 89789-48-0; **3f**, 89789-49-1; **3g**, 89789-50-4; **3h**, 89789-51-5; **3i**, 89789-52-6; CH_3CO_2H, 64-19-7; $CH_3CH_2CO_2H$, 79-09-4; $(CH_3)_2CHCO_2H$, 79-31-2; $CH_3(CH_2)_2CO_2H$, 107-92-6; $CH_3(CH_2)_3CO_2H$, 109-52-4.

Photoinduced Electron-Transfer Processes Involving Substituted Stilbene Oxides[1]

P. K. Das,*[†] A. J. Muller,[‡] and G. W. Griffin*[‡]

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and the Chemistry Department, University of New Orleans, New Orleans, Louisiana 70148

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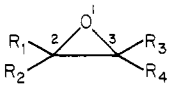
Electron-transfer interactions of several substituted stilbene oxides (oxiranes) containing cyano and carbomethoxy groups at 2,3-positions with the singlet and triplet states of 1,4-dicyanonaphthalene (DCN) and *N,N,N′,N′*-tetramethylbenzidine (TMB) have been investigated by steady-state fluorescence quenching, pulse radiolysis, and laser flash photolysis. The results are examined in the context of the behaviors of the oxiranes with respect to photosensitized isomerization and degradation under steady-state irradiation (350 nm). Transient spectra concerning radical ions and triplets of DCN and TMB as well as primary photoproducts observed in the photosensitization of some of the oxiranes are presented. Evidence for charge-transfer interaction with oxiranes in acetonitrile is obtained from transient-absorption spectral characterization of the radical anion of DCN and the radical cation of TMB; the efficiency of net electron transfer forming solvated radical ions is very small (0–0.3). No transient phenomena attributable to ylides formed via back electron transfer within an ion pair or between solvated radical ions are observed. With trans and cis forms of 2,3-dicarbomethoxy-2,3-bis(4-methoxyphenyl)oxirane, long-lived radical cations with dual absorption maxima at 400 and 580 nm are formed as a result of photosensitization by DCN in acetonitrile. The radical cation from the cis oxirane displays a relatively slow growth ($t_{1/2}$ = 350 ns) for its formation from a charge-transfer-derived precursor with a single absorption maximum at 460 nm; this transient behavior appears to be associated with either relatively slow ring opening of an initially formed, closed ring, radical cation of the cis oxirane via intramolecular electron transfer, or isomerization of an initially formed, open ring, strained configuration to a stable one derivable by electron transfer from the trans oxirane.

Introduction

Organic reactions mediated by charge-transfer interactions from electronically excited states are of current interest. Vicinal diaryl-substituted oxiranes undergo ring opening to carbonyl ylides[2] upon direct irradiation and our experience in this area provided the incentive for the present study[3] of the reactions of radical ions of such oxiranes presumably generated by photoinduced electron-transfer processes in solution. The importance of charge transfer has been recognized in the photochemical isomerization[4a,5] of arylcyclopropanes and in the photochemical addition[4b] of methanol to these systems; cyanoaromatics have been used as electron-transfer sensitizers (excited-state acceptors) in these studies. Albini and Arnold[6] have studied photosensitized isomerization of *cis*- and *trans*-2,3-diphenyloxiranes using a variety of acceptors and proposed a mechanism involving singlet-mediated formation and cleavage of oxirane radical cation followed by back electron transfer from the sensitizer radical anion to produce a carbonyl ylide. The intermediacy of the ylide was based on the results concerning its trapping by various dipolarophiles. More recently, Leslie and Trozzolo[7] observed that following laser excitation (337.1 nm) into a low-lying charge-transfer absorption band of the 1,4-dicyanobenzene and 2,3-diphenyloxirane system in acetonitrile the transient species characterized as a radical cation of the oxirane decayed much more rapidly than the radical anion of 1,4-dicyanobenzene (presumably to a ring closed form with the positive charge localized on oxygen or a phenyl ring).

In this paper we present the results of an investigation of electron-transfer interactions of several oxiranes with 1,4-dicyanonaphthalene (DCN) and *N,N,N′,N′*-tetramethylbenzidine (TMB), which play the roles of excited-

Chart I



1a, $R_1 = R_4 = CN; R_2 = R_3 = p\text{-}CH_3OC_6H_4$
1b, $R_1 = R_4 = CN; R_2 = R_3 = p\text{-}CH_3C_6H_4$
1c, $R_1 = R_4 = CN; R_2 = R_3 = C_6H_5$
2a, $R_1 = R_3 = COOMe; R_2 = R_4 = p\text{-}CH_3OC_6H_4$
2b, $R_1 = R_3 = COOMe; R_2 = R_4 = p\text{-}CH_3C_6H_4$
2c, $R_1 = R_3 = COOMe; R_2 = R_4 = C_6H_5$
3a, $R_1 = R_4 = COOMe; R_2 = R_3 = p\text{-}CH_3OC_6H_4$
3b, $R_1 = R_4 = COOMe; R_2 = R_3 = p\text{-}CH_3C_6H_4$

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[2] (a) Becker, R. S.; Bost, R. O.; Kolc, J.; Bertoniere, N. R.; Smith, R. L.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1302–1311. (b) Do-Minh, T.; Trozzolo, A. M.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1402–1403. (c) Wong, J. P. K.; Fahmi, A. A.; Griffin, G. W.; Bhacca, N. S. *Tetrahedron* **1981**, *37*, 3345–3355.

[3] Preliminary papers on part of this work were presented: (a) Griffin, G. W. 64th Chemical Conference and Exhibition, Chemical Institute of Canada, Halifax, Nova Scotia, May 31–June 3, 1982. (b) Griffin, G. W. 10th International Conference on Photochemistry, University of Crete, Crete, Greece, Sept. 6–12, 1982. (c) Griffin, G. W.; Muller, A. J.; Reichel, L. W.; Tamvakis, A. P.; Timpa, J. D. 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 28–April 2, 1982. (d) Griffin, G. W.; Muller, A. J.; Reichel, L. W.; Tamvakis, A. P.; Timpa, J. D. Symposium on Pure and Applied Photochemistry in conjunction with the 65th Annual Chemical Institute of Canada Meeting, Toronto, Canada, May 30–June 2, 1982. (e) Griffin, G. W.; Muller, A. J.; Reichel, L. W.; Tamvakis, A. P.; Timpa, J. D. IX IUPAC Symposium on Photochemistry, Pau, France, July 25–30, 1982. (f) Das, P. K.; Muller, A. J.; Griffin, G. W.; Gould, I. R.; Tung, C. H.; Turro, N. J. *Photochem. Photobiol.* **1984**, *39*, 281–285.

[†] University of Notre Dame.

[‡] University of New Orleans.

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