

Time-resolved IR studies of α -lactones[†]

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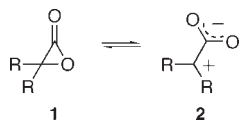
ABSTRACT: A series of α -lactones were generated from the reaction of phenylchlorocarbene, 4-nitrophenylchlorocarbene, diphenylcarbene, bis(4-nitrophenyl)carbene and bis(4-methoxyphenyl)carbene with carbon dioxide and examined by nanosecond time-resolved infrared (TRIR) spectroscopy. Estimated second-order rate constants for the reaction of these carbenes with carbon dioxide indicate that more nucleophilic carbenes react at faster rates, in agreement with previous low-temperature matrix experiments. Spectral TRIR data confirms that the structure of α -lactones is dependent both on substituents at the α -carbon and on solvent polarity, with electron-donating substituents and polar solvents favoring a zwitterionic ring-opened structure as opposed to the three-membered ring oxiranone form. B3LYP calculations using self-consistent reaction field (SCRF) methods also provide support for these experimental investigations. Copyright © 2004 John Wiley & Sons, Ltd.

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KEYWORDS: α -lactones; oxiranones; time-resolved infrared spectroscopy; phenylchlorocarbene; 4-nitrophenylchlorocarbene; diphenylcarbene; bis(4-nitrophenyl)carbene; bis(4-methoxyphenyl)carbene

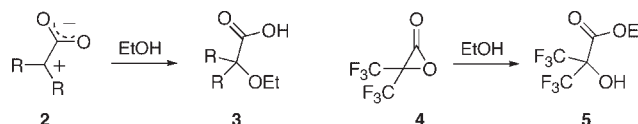
INTRODUCTION

α -Lactones (oxiranones) (**1**) are three-membered heterocyclic rings that have been invoked as intermediates in a variety of organic transformations¹ and in enzymatic glycosyltransferase reactions.² Most α -lactones are unstable at room temperature;³ those that are stable require bulky⁴ or strongly electron-withdrawing substitution⁵ at the α -carbon. Much of the chemistry of α -lactones has been explained by invoking a higher energy ring-opened zwitterionic form (**2**). The relative stability of ring-closed form **1** vs ring-opened form **2** is dependent on the substituents R. Calculations have predicted that for the parent α -lactone (R=H), ring-closed form **1** is significantly lower in energy than ring-opened form **2**.^{6–8} Calculations have also shown that, as expected, substitution with electron-donating R groups, and also polar solvation, preferentially stabilize **2**.⁹



Nucleophilic attack of alcohols (e.g. ethanol) on α -lactones gives different regiochemistry depending on the

substituent R. In cases where R is alkyl or phenyl, ethanol reacts with α -lactones to produce α -ethoxy acids (**3**), presumably via zwitterionic form **2**.^{10–12} When R is the strongly electron-withdrawing trifluoromethyl group (such as in **4**), however, ethanol reacts to produce an α -hydroxy ester (**5**), which presumably is formed by attack on ring-closed form **1**.⁵ The trifluoromethyl groups obviously destabilize the dipolar ring-opened structure.



α -Lactones readily undergo decarbonylation and also polymerization reactions. Loss of carbon monoxide most likely occurs through ring-closed form **1**, whereas polymerization occurs through ring-opened form **2**. Hence structures **1** and **2** both play important roles in α -lactone chemistry; however, in essentially all cases where ring-opened form **2** dominates the observed reactivity, it has not been detected spectroscopically. (We are aware of only one instance in which zwitterion **2** has been directly observed;¹³ this study will be discussed in more detail below.) For example, the reactivity of α -lactones **6** and **7**, even at temperatures as low as -100°C , is consistent with ring-opened form **2**.^{10–12} However, low-temperature (77 or 10 K) matrix IR spectroscopy of **6** ($\nu_{\text{C=O}} = 1900\text{ cm}^{-1}$)¹¹ and **7** ($\nu_{\text{C=O}} = 1890\text{ cm}^{-1}$)^{14,15} has revealed carbonyl stretching modes at considerably high frequencies, indicative of ring-closed form **1**. These observations have been rationalized in terms of a small energy gap between structure **1** and its more reactive, but

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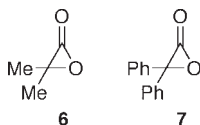
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[†]Dedicated to Professor Kurt Mislow on the occasion of his 80th birthday.

higher energy counterpart **2**, and are consistent with previous computational work.



Since the IR signatures of structures **1** and **2** are expected to be different, we generated a series of α -lactones and report here their characterization by nanosecond time-resolved infrared (TRIR) spectroscopy. We examined the influence of substituents (**R**) and solvent on the relative stability of **1** and **2**. These experimental investigations were supported by B3LYP calculations using self-consistent reaction field (SCRf) methods.

RESULTS AND DISCUSSION

α -Lactones were generated from the reaction of carbenes with carbon dioxide and examined by TRIR spectroscopy. (This method of α -lactone generation has been used by Kistiakowsky and Sauer in the gas phase,¹⁶ by Wheland and Bartlett in solution¹² and by both Milligan and Jacox¹⁷ and Sander and co-workers^{14,15} in low-temperature matrices; Kovacs and Jackson reported a comprehensive computational investigation of the reaction of methylene with CO₂.¹⁸) Representative TRIR data for the reaction of phenylchlorocarbene (**9**), produced by laser photolysis of phenylchlorodiazirine (**8**), with CO₂ in dichloromethane are shown in Figs 1 and 2. Depletion of reactants gives rise to negative signals and the formation of transient intermediates or products leads to positive bands. The negative signal at 1566 cm⁻¹ is assigned to depletion of diazirine **8**, whereas the positive bands at 1586, 1910 and 1776 cm⁻¹ are assigned to carbene **9**,¹⁵ α -lactone **10**¹⁵ and acid chloride **11**,¹⁹ respectively, based on previous studies (Scheme 1).^{15,20}

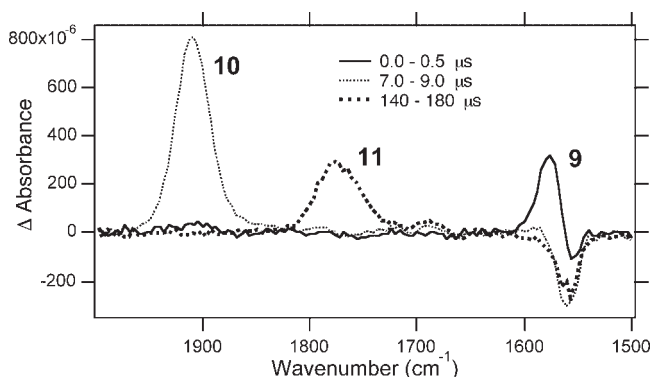


Figure 1. TRIR difference spectra averaged over the time-scales indicated following 355 nm laser photolysis of diazirine **8** (15.7 mm) in CO₂-saturated dichloromethane

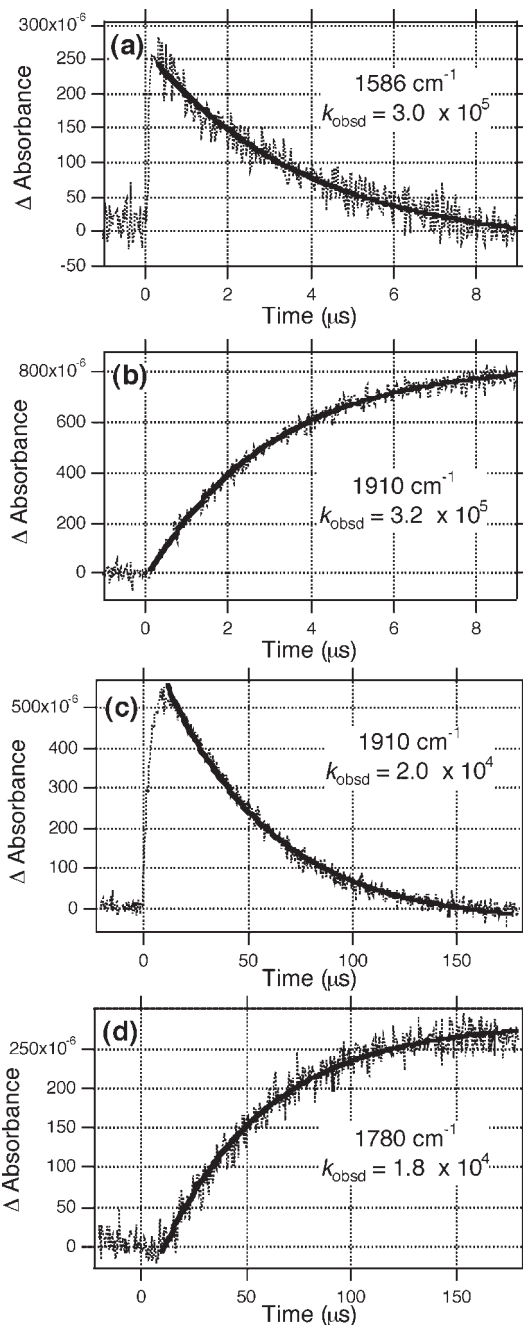
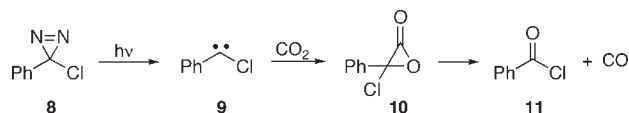


Figure 2. Representative kinetic traces observed following 355 nm laser photolysis of diazirine **8** (15.7 mm) in CO₂-saturated dichloromethane showing (a) decay of carbene **9**, (b) growth of α -lactone **10**, (c) decay of α -lactone **10** and (d) growth of acid chloride **11**. The dotted curves are experimental data; the solid curves are the calculated best fit to a single exponential function

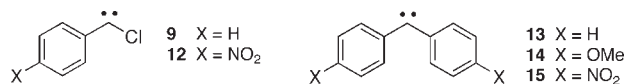


Scheme 1

Consistent with Scheme 1, we observe (1) depletion of the diazirine and formation of the carbene within the time resolution (50 ns) of our experiment, (2) subsequent decay of the carbene ($k_{\text{osbd}} = 3.0 \times 10^5 \text{ s}^{-1}$) at the same rate within experimental error ($\pm 10\%$) that the α -lactone is produced ($k_{\text{osbd}} = 3.2 \times 10^5 \text{ s}^{-1}$) and (3) final decay of the α -lactone ($k = 2.0 \times 10^4 \text{ s}^{-1}$) at the same rate as the acid chloride product is formed ($k_{\text{osbd}} = 1.8 \times 10^4 \text{ s}^{-1}$). The position of the α -lactone band at 1910 cm^{-1} is clearly indicative of ring-closed form **1** and in very good agreement with the signal observed at 10 K (1920 cm^{-1}) by Sander and co-workers.¹⁵

Sander and co-workers also previously examined the effects of carbene spin state and philicity on the carboxylation reaction in low-temperature matrices.¹⁵ They concluded that the reactivity of carbenes towards CO_2 is determined by their philicity (more nucleophilic carbenes are more reactive) and that carbene spin state interestingly has little effect. Kovacs and Jackson suggested that this reactivity pattern may be explained by a non-equilibrium surface crossing mechanism.¹⁸

Using the pseudo-first-order equation $k_{\text{obsd}} = k_0 + k_{\text{CO}_2}[\text{CO}_2]$ (where k_{CO_2} is the second-order rate constant for the reaction of carbene with CO_2 and k_0 is the rate of carbene decay in the absence of CO_2), we estimated solution-phase values of k_{CO_2} for phenylchlorocarbenes **9** and **12** and diphenylcarbenes **14** and **15** in dichloromethane (Table 1). (The concentration of CO_2 in saturated dichloromethane solution at 25°C and 1 atm is 196 mmol l^{-1} .²¹) The trend of these estimated second-order rate constants agrees with that observed in low-temperature matrices by Sander and co-workers. Although this series of carbenes contains both ground-state singlets (**9** and **12**) and ground-state triplets (**13**–**15**), unlike in Sander and co-workers' low-temperature experiments,^{14,15} we cannot rule out the thermal population of and reaction from the higher spin state in our room temperature studies.



Although carbene **15** is unreactive with CO_2 , TRIR data were obtained for the reaction of carbenes **9**, **12**–**14** with CO_2 ; the experimentally observed C=O stretching frequencies are given in Table 1. Spectral data for the α -lactone derived from carbene **12** (see Supplementary material), although significantly weaker in intensity, are analogous to those derived from carbene **9**. The TRIR spectra for the α -lactones derived from carbenes **13** and **14**, however, are dramatically different from each other (Fig. 3). Whereas the product of CO_2 reaction with **13** in dichloromethane is clearly the ring-closed α -lactone **16** ($\nu_{\text{C=O}} = 1880 \text{ cm}^{-1}$, again in good agreement with that observed by low-temperature matrix IR spectroscopy¹⁴ at 1890 cm^{-1}), the carboxylation of **14** in the same solvent leads to a structure that appears to be best described by

Table 1. Estimated second-order rate constants for carbene reactions with CO_2 in dichloromethane and IR frequencies of the corresponding α -lactones

Carbene	k_{CO_2} ($\text{l mol}^{-1} \text{ s}^{-1}$)	α -Lactone (cm^{-1})
9	1×10^6	1910
12	2×10^5	1920
13	— ^a	1880
14	2×10^7	1620, 1576
15	$<10^4$	— ^b

^a A carbene band is not observed in dichloromethane owing to overlap with a diazo precursor depletion band.

^b Carbene **15** is unreactive with CO_2 ; no α -lactone signals are observed.

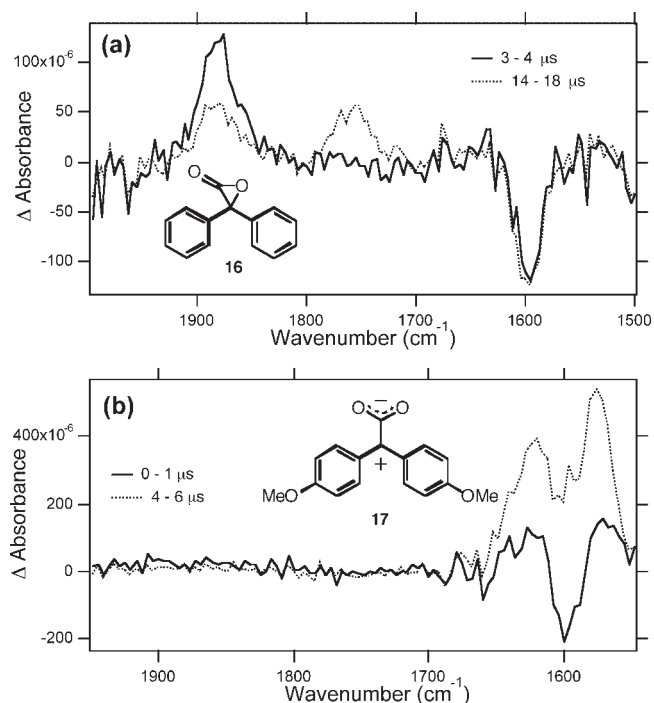
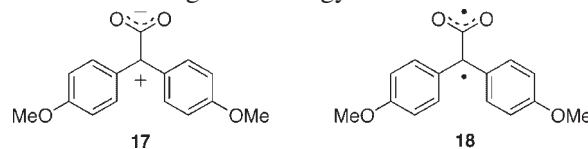


Figure 3. TRIR difference spectra averaged over the time-scales indicated following 266 nm photolysis of (a) diphenyldiazomethane (3.6 mm) and (b) bis(4-methoxyphenyl)diazomethane (1.1 mm) in CO_2 -saturated dichloromethane

zwitterion **17**. In this latter case [Fig. 3(b)], the spectral region between 1800 and 2000 cm^{-1} is devoid of any signal that may be attributed to the ring-closed form. Instead, intense IR bands are detected at 1620 and 1576 cm^{-1} , consistent with B3LYP/6–31G(d) optimized geometries (all calculations were carried out with the Gaussian suite of programs²²) (Fig. 4 and Supplementary material) and calculated frequencies (scaled by 0.96)²³ (Table 2). Indeed, even geometry minimizations starting from the ring-closed form of **17** resulted in a ring-opened minimum. In addition, B3LYP/6–31G(d) calculations indicate that the corresponding triplet-biradical **18** is $16.1 \text{ kcal mol}^{-1}$ higher in energy than zwitterion **17**.



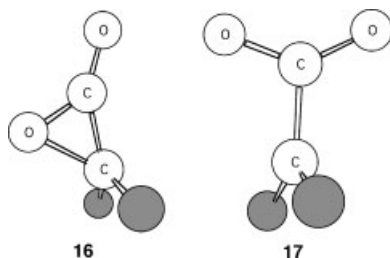


Figure 4. B3LYP/6–31G(d)-calculated geometries of diphenyloxiranone (**16**) and bis(4-methoxyphenyl)oxiranone (**17**). The aryl groups have been removed for clarity

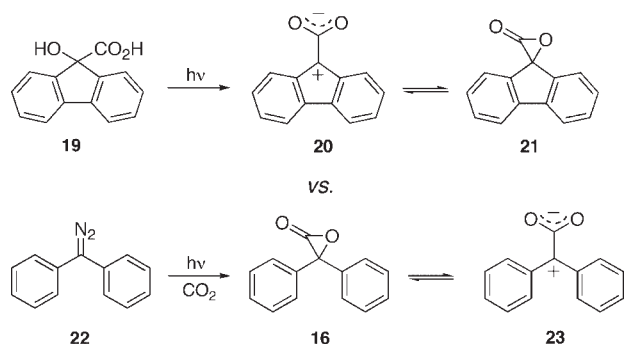
Table 2. Selected experimental and B3LYP/6–31G(d)-calculated IR frequencies (scaled by 0.96) for diphenyloxiranone (**16**) and bis(4-methoxyphenyl)oxiranone (**17**)

α -Lactone	Experimental (cm ⁻¹)	Calculated (cm ⁻¹)	Assignment
16	1880	1907	Carbonyl str.
17	1576	1587	Phenyl C–C str.
		1597	Phenyl C–C str.
	1620	1658	Asym. C–O str.

Lew *et al.*¹³ photolyzed 9-hydroxy-9-fluorene-carboxylic acid in hexfluoro-2-propanol (HFIP) and detected a transient ($\tau \approx 20 \mu\text{s}$) with $\lambda_{\text{max}} = 495 \text{ nm}$ and strong IR bands at 1575, 1600, and 1620 cm⁻¹, which was assigned to zwitterion **20**, in excellent agreement with our measured IR bands for ring-opened form **17** (Scheme 2). They examined the region 1988–1855 cm⁻¹ and reported that no signals were observed for ring-closed form **21**.

The difference in structure between **16** and **17** is readily understood in terms of the addition of strongly electron-donating substituents, but the contrast between **16** and **20** is less easily rationalized. Photolysis of **19** was carried out in HFIP [dielectric constant (ϵ) = 16.75] whereas the TRIR experiments were carried out in dichloromethane ($\epsilon = 9.08$), suggesting that the α -lactone structure is dependent on solvent polarity.

We examined, both experimentally and computationally, the role of solvent polarity on the stabilization of



Scheme 2

zwitterionic form **2**. TRIR results observed following photolysis of diphenyldiazomethane (**22**) in acetonitrile-*d*₃ (Fig. 5) contain signals that can be attributed to both ring-closed form **16** and ring-opened form **23**. SCRF B3LYP/6–31G(d) calculations using the Onsager model^{24,25} for acetonitrile ($\epsilon = 35.9$) predict that ring-closed form **16** is 2.6 kcal mol⁻¹ (1 kcal = 4.184 kJ) more stable than ring-opened form **23**. Strong IR bands are predicted at 1886 cm⁻¹ for **16** (in good agreement with the experimentally observed 1880 cm⁻¹ band) and at 1314 cm⁻¹ for **23** (in reasonable agreement with the experimentally observed 1356 cm⁻¹ band). Less intense IR bands are also predicted at 1638 and 1577 cm⁻¹ for **23**. (See Supplementary material for a complete tabulation of computational results obtained for **16** and **23**.) These calculated bands are probably obscured by an overlapping diazo depletion band at 1592 cm⁻¹ in the experimental data.

The kinetics observed for the 1880 cm⁻¹ band of **16** and the 1356 cm⁻¹ band of **23** are in good agreement with each other, indicating that these two species are in equilibrium (**16**, $k_{\text{growth}} = 1.5 \times 10^6 \text{ s}^{-1}$, $k_{\text{decay}} = 1.1 \times 10^5 \text{ s}^{-1}$; **23**, $k_{\text{growth}} = 1.2 \times 10^6 \text{ s}^{-1}$, $k_{\text{decay}} = 1.2 \times 10^5 \text{ s}^{-1}$). Given that we can observe an equilibrium mixture of **16** and **23**, the calculated energy difference of 2.6 kcal mol⁻¹ between the two is almost certainly overestimated.

TRIR data observed following photolysis of **22** in cyclohexane (Fig. 6) contains a band easily attributed to ring-closed form **16**, but in contrast to data obtained in acetonitrile, no signals indicating the presence of ring-opened form **23**. SCRF B3LYP/6–31G(d) calculations using the Onsager model^{24,25} for cyclohexane ($\epsilon = 2.02$) predict a strong IR band at 1900 cm⁻¹, in excellent agreement with the experimentally observed band. These calculations, however, indicate that ring-opened form **23** is not a minimum on the potential energy surface, but rather a transition-state structure (one imaginary frequency = 72 cm⁻¹). The calculated frequencies for this structure (Supplementary material) are, however, similar to those obtained in the acetonitrile calculations.

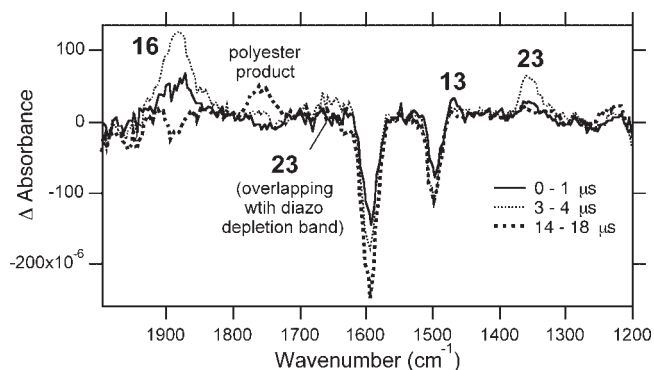


Figure 5. TRIR difference spectra averaged over the time-scales indicated following 266 nm laser photolysis of diphenyldiazomethane (**22**) (9.8 mm) in CO₂-saturated acetonitrile-*d*₃

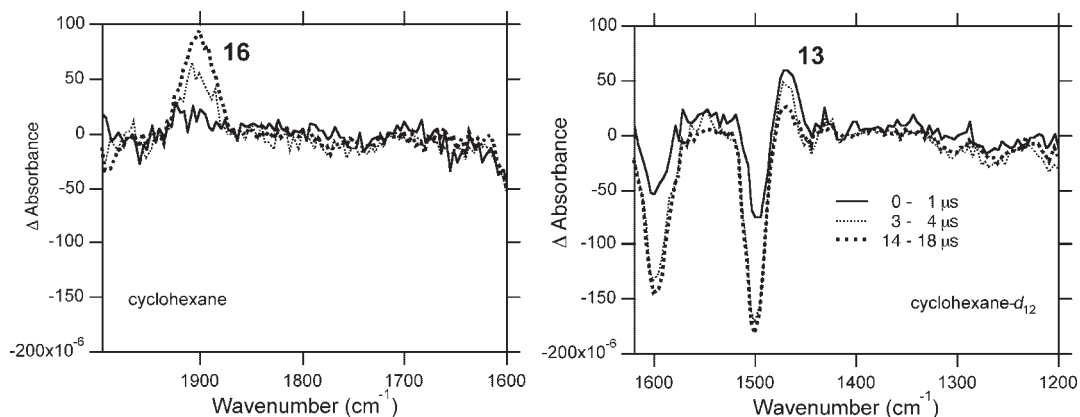


Figure 6. TRIR difference spectra averaged over the time-scales indicated following 266 nm laser photolysis of diphenyldiazomethane (**22**) (6.3 mm) in CO₂-saturated cyclohexane and cyclohexane-*d*₁₂. Since the detection of transient species is more problematic in regions with strong solvent bands owing to the low transmission of IR light, cyclohexane-*d*₁₂ was required for the spectral region below 1600 cm⁻¹.

CONCLUSIONS

TRIR spectroscopy was used to characterize a series of α -lactone intermediates and provided direct information concerning their structure in solution. The structure of α -lactones, as reflected in the observed TRIR spectra, is dependent both on the substituents at the α carbon and on solvent polarity, with electron-donating substituents and polar solvents favoring a zwitterionic ring-opened structure. B3LYP calculations using SCRF methods to account for solvent polarity are consistent with these experimental conclusions. We are currently extending our TRIR studies to the investigation of α -lactam intermediates.

EXPERIMENTAL

Phenylchlorodiazirine (**1**),²⁶ 4-nitrophenylchlorodiazirine,²⁷ diphenyldiazomethane,²⁸ bis(4-nitrophenyl)diazomethane,²⁹ and bis(4-methoxyphenyl)diazomethane³⁰ were prepared according to literature procedures.

We conducted TRIR experiments following the method of Hamaguchi and co-workers³¹ as described previously.³² Briefly, the broadband output of an MoSi₂ IR source (JASCO) is crossed with excitation pulses from an Nd:YAG laser. Changes in IR intensity are monitored by an MCT photovoltaic IR detector (Kolmar Technologies, KMPV11-1-J1), amplified and digitized with a Tektronix TDS520A oscilloscope. The experiment was conducted in the dispersive mode with a JASCO TRIR-1000 spectrometer. TRIR difference spectra were collected at 16 cm⁻¹ resolution using either a Continuum HPO-300 diode-pumped Nd:YAG laser (266 nm, 10 ns, 0.4 mJ; 355 nm, 12 ns, 0.6 mJ) or a Quantronix Q-switched Nd:YAG laser (266 nm, 90 ns, 0.4 mJ; 355 nm, 90 ns, 1.5 mJ), both operating at 200 Hz. Kinetic traces were collected using a Continuum Minilite II Nd:YAG laser (266 nm, 5 ns, 1–4 mJ; 355 nm, 5 ns, 2–8 mJ) operating

at 20 Hz or the Quantronix Q-switched Nd:YAG laser operating at 200 Hz.

Supplementary material

TRIR data for 4-nitrophenylcarbene and tabulations of optimized Cartesian coordinates, total energies, and calculated frequencies and intensities are available in Wiley Interscience.

Acknowledgments

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REFERENCES

- (a) Niwayama S, Noguchi H, Ohno M, Kobayashi S. *Tetrahedron Lett.* 1992; **34**: 665–668; (b) Schmittel M, von Seggern H. *Liebigs Ann. Chem.* 1995; 1815–1821; (c) Strijtveen B, Kellogg RM. *Recl. Trav. Chim. Pays-Bas* 1987; **106**: 539–542; (d) Adam W, Blancafort L. *J. Am. Chem. Soc.* 1996; **118**: 4778–4787.
- (a) Ashwell M, Guo XM, Sinnott ML. *J. Am. Chem. Soc.* 1992; **114**: 10158–10166; (b) Chong AKJ, Pegg MS, Taylor NR, Vonitzstein M. *Eur. J. Biochem.* 1992; **207**: 335–343; (c) Guo XM, Sinnott ML. *Biochem. J.* 1993; **296**: 291–292; (d) Guo XM, Laver WG, Vimr E, Sinnott ML. *J. Am. Chem. Soc.* 1994; **116**: 5572–5578; (e) Horenstein BA, Bruner M. *J. Am. Chem. Soc.* 1996; **118**: 10371–10379; (f) Horenstein BA. *J. Am. Chem. Soc.* 1997; **119**: 1101–1107.
- L'abbé G. *Angew. Chem., Int. Ed. Engl.* 1980; **19**: 276–289.
- Coe PL, Sellers A, Tatlow JC, Whittaker G, Fielding HC. *J. Chem. Soc., Chem. Commun.* 1982; 362–363.
- Adam W, Liu J, Rodriguez O. *J. Org. Chem.* 1973; **38**: 2269–2270.

6. Liebman JF, Greenberg A. *J. Org. Chem.* 1974; **39**: 123–130.
7. Chung CSC. *J. Mol. Struct.* 1976; **30**: 189–191.
8. Antolovic D, Shiner VJ, Davidson ER. *J. Am. Chem. Soc.* 1988; **110**: 1375–1381.
9. (a) Firth-Clark S, Rodriquez CF, Williams IH. *J. Chem. Soc., Perkin Trans. 2* 1997; 1943–1948; (b) Ruggiero GD, Williams IH. *J. Chem. Soc., Perkin Trans. 2* 2001; 733–737; (c) Buchanan JG, Charlton MH, Mahon MF, Robinson JJ, Ruggiero GD, Williams IH. *J. Phys. Org. Chem.* 2002; **15**: 642–646.
10. Adam W, Rucktäschel R. *J. Am. Chem. Soc.* 1971; **93**: 557–559.
11. Chapman OL, Wojtkowski PW, Adam W, Rucktäschel RR. *J. Am. Chem. Soc.* 1972; **94**: 1365–1367.
12. Wheland R, Bartlett PD. *J. Am. Chem. Soc.* 1970; **92**: 6057–6058.
13. Lew CSQ, Wagner BD, Angelini MP, Lee-Ruff E, Luszyk J, Johnston LJ. *J. Am. Chem. Soc.* 1996; **118**: 12066–12073.
14. Sander WW. *J. Org. Chem.* 1989; **54**: 426–427.
15. Wierlacher S, Sander W, Liu MTH. *J. Org. Chem.* 1992; **57**: 1051–1053.
16. Kistiakowsky GB, Sauer K. *J. Am. Chem. Soc.* 1958; **80**: 1066–1071.
17. Milligan DE, Jacox ME. *J. Chem. Phys.* 1962; **36**: 2911–2917.
18. Kovacs D, Jackson JE. *J. Phys. Chem. A* 2001; **105**: 7579–7587.
19. Pouchert CJ (ed). *The Aldrich Library of Infrared Spectra* (3rd edn). Aldrich Chemical: Milwaukee, WI, 1981; 1057.
20. Ganzer GA, Sheridan RS, Liu MTH. *J. Am. Chem. Soc.* 1986; **108**: 1517–1520.
21. Fogg PGT (ed). *Carbon Dioxide in Non-aqueous Solvents at Pressures Less Than 200 kPa*. Pergamon Press: Oxford, 1992; 259.
22. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA. *Gaussian 98, Revision A.7*. Gaussian: Pittsburgh, PA, 1998.
23. Scott AP, Radom L. *J. Phys. Chem.* 1996; **100**: 16502–16513.
24. Wong MW, Frisch MJ, Wiberg KB. *J. Am. Chem. Soc.* 1991; **113**: 4776–4782.
25. Wong MW, Wiberg KB, Frisch M. *J. Chem. Phys.* 1991; **95**: 8991–8998.
26. Graham WH. *J. Am. Chem. Soc.* 1965; **87**: 4396–4397.
27. Liu MTH, Toriyama K. *Can. J. Chem.* 1972; **50**: 3009–3016.
28. Smith LI, Howard KL. *Org. Synth., Coll. Vol.* 1955; **3**: 351–352.
29. Just G, Wang ZY, Chan L. *J. Org. Chem.* 1988; **53**: 1030–1033.
30. Kimse W, Kilian J, Steen S. *J. Am. Chem. Soc.* 1990; **112**: 6399–6400.
31. (a) Iwata K, Hamaguchi H. *Appl. Spectrosc.* 1990; **44**: 1431–1437; (b) Yuzawa T, Kato C, George MW, Hamaguchi H. *Appl. Spectrosc.* 1994; **48**: 684–690.
32. Wang Y, Yuzawa T, Hamaguchi H, Toscano JP. *J. Am. Chem. Soc.* 1999; **121**: 2875–2882.