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Stable Carbonyl O-oxides and Dioxiranes

K. Schroeder, K. Block, W. Kappert, and W. Sander*

Lehrstuhl für Organische Chemie II der Ruhr-Universität,
Universitätsstraße 150, D-44780 Bochum, Germany

E-mail: sander@xenon.orch.ruhr-uni-bochum.de

Homepage: <http://neon.orch.ruhr-uni-bochum.de/sander>

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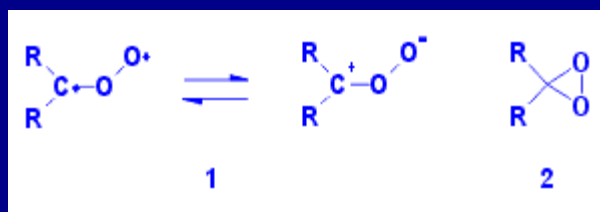
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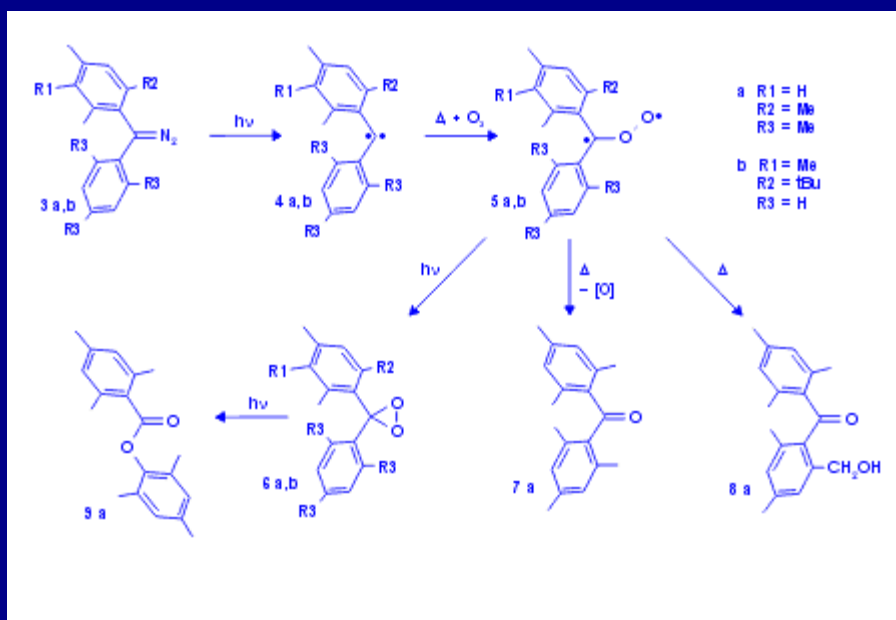
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1. Introduction

The transfer of oxygen atoms plays an important role in organic chemistry. Carbonyl oxides **1** and the isomer dioxiranes **2** are discussed as short-lived intermediates in decomposition processes, oxidations of organic compounds (Baeyer-Villiger Reaction, Ozonolysis), and enzymatic processes ^{1, 2, 3}. During the last years **2** have been used as selective oxygen transfer reagents ^{4, 5, 6, 7, 8, 9}. A successful technique for the stabilization of reactive molecules is the introduction of sterically demanding groups such as *t*-butyl or mesityl. While several derivatives of dioxiranes **2** could be synthesized and characterized in solution, carbonyl oxides **1** are in general transient species.



Here we describe the preparative scale synthesis of carbonyl O-oxides **5a** and **5b** via oxidation of carbenes **4**. Further irradiation leads to dioxiranes **6a** and **6b**. Dimesityl ketone O-oxide **5a** was characterized by NMR spectroscopy in solution at low temperature. Dimesityldioxirane **6a** forms a colorless crystalline material that could be characterized by x-ray structure analysis ^{10, 11}



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2. Synthesis of Carbonyl O-oxides

Diazo compounds **3a** and **3b** were irradiated with $\lambda > 515$ and 495 nm in oxygen saturated CCl_3F or in 1 : 1 mixtures of $\text{CCl}_3\text{F}/(\text{CBrF}_2)_2$ at low temperatures. The absorption maxima of the intense yellow solutions were at 398 and 394 nm. The yield of **5a** is estimated to 20 - 25 %. As expected, **5a** is very photolabile and irradiation with $\lambda > 475$ nm rapidly results in the decolorization of the solution and formation of dioxirane **6a** as the major product (Scheme 1) ^{10, 12}. Alternatively, carbonyl oxide **5a** was synthesized by the reaction of diazo compound **3a** with $^1\text{O}_2$ in a variety of solvents with small amounts of photosensitizers. Good results were obtained in CCl_3F / octafluoroporphyrin, THF / rose bengal, or pentane / C_{60} at temperatures below -80°C and $\lambda > 570$ nm excitation. Carbonyl oxide **5a** is the first carbonyl oxide that could be characterized by ^1H and - after ^{13}C isotopic labeling - ^{13}C NMR spectroscopy. The chemical shift of the "carbonyl" carbon atom of **5a** was found at 211.0 ppm ¹⁰.

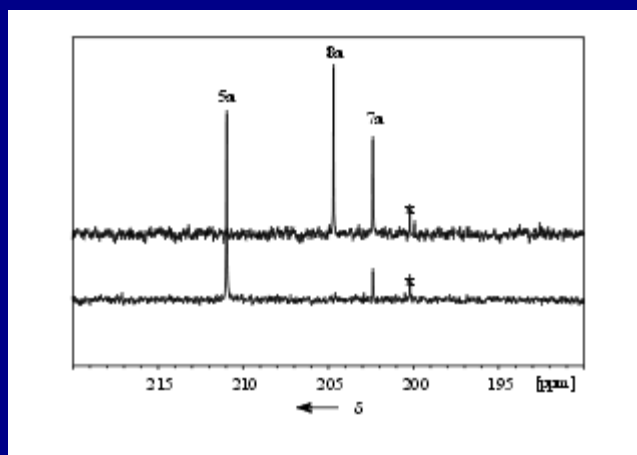


Figure 1: ^{13}C -NMR spectra showing the thermal reaction of **5a** to produce **7a** and **8a**.

Bottom: Spectrum produced by irradiation ($\lambda > 515$ nm) of ^{13}C -**3a** in O_2 saturated $\text{CFCl}_3/(\text{CBrF}_2)_2$ at 77K and subsequent warming to -70°C .

Top: Same as bottom, but additional warming to room temperature and re-cooling to -70°C .

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3. Thermal Decay of Carbonyl O-oxides

At - 80° C carbonyl oxide **5a** is thermally stable, while above -50° C a rapid decay following first order kinetics with an activation enthalpy at 300 K of $13.3 \pm 1 \text{ kcal mol}^{-1}$ is observed. The major products of the decay of **5a** are dimesitylketone **7a**, formed by loss of the terminal oxygen atom, or the benzyl alcohol **8a**, the insertion product of an oxygen atom into one of the ortho methyl groups (Scheme 1) ¹⁰. The decay of **5b** follows first order kinetics, the products have not yet been identified. The halve lifetime of **5a** and **5b** in $\text{CCl}_3\text{F}/(\text{CBrF}_2)_2$ (1:1) drops from 38 min at - 82° C to just 3.5 min at - 60° C (Figure 2), which corresponds to an activation enthalpy of $5.8 \text{ kcal mol}^{-1}$. Thus, **5b** is considerably less stable than **5a** with half lifetimes of 8250 min and 62 min at the same temperatures and an activation enthalpy for the thermal decay of $13.3 \text{ kcal mol}^{-1}$. Obviously, the less efficient shielding of the phenyl substituent in **5b** - compared to the mesityl group in **5a** - is not compensated by the additional t-butyl group in the second aryl ring.

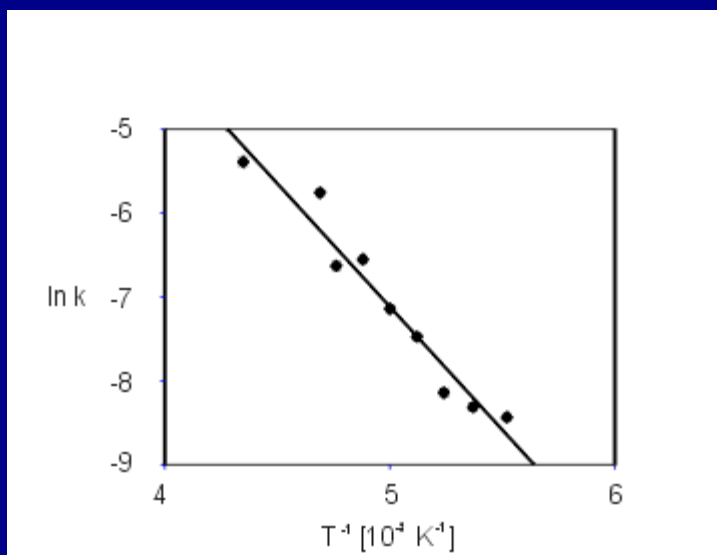


Figure 2: Arrhenius plot of the thermal decay of carbonyl oxide **5b** in $\text{CCl}_3\text{F}/(\text{CBrF}_2)_2$ (1:1).

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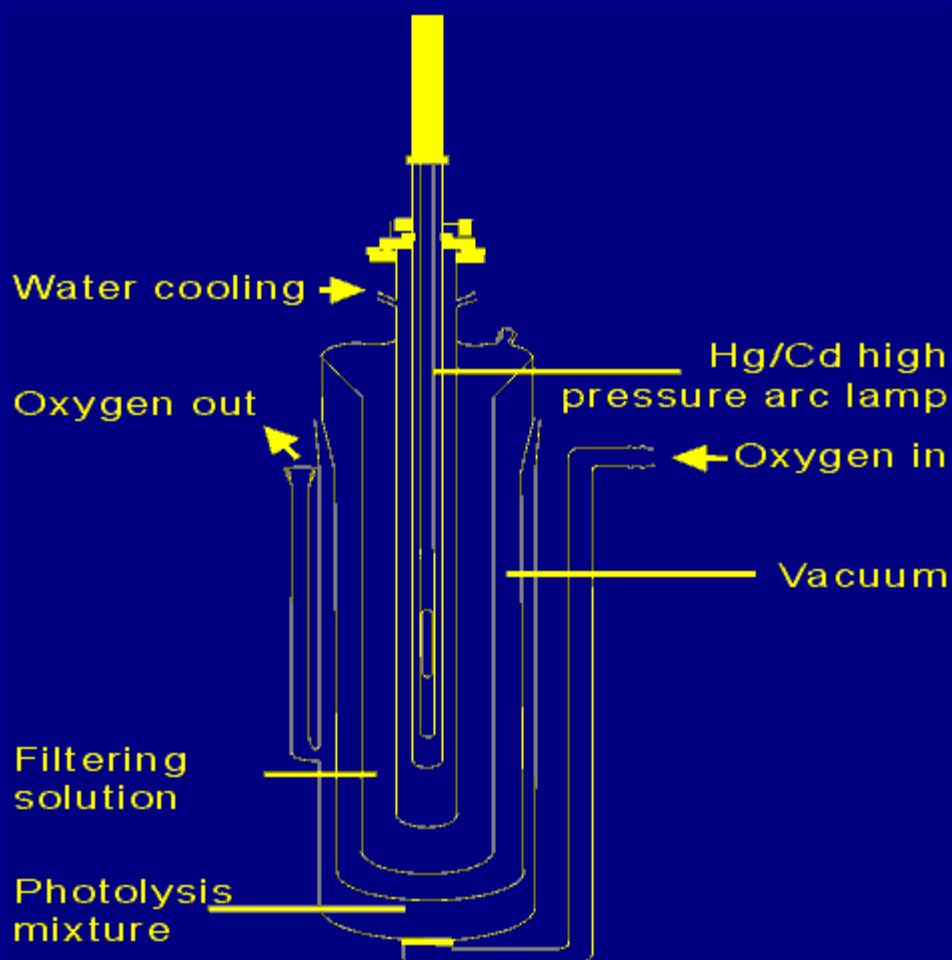
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- [4] Kafafi, S. A.; Martinez, R. I.; Herron, J. T. *Mol. Struct. Energ.* 1988, 6, 283.

4. Synthesis of Dimesityldioxirane

A general route to generate dioxiranes is the oxidation of triplet carbenes with molecular oxygen $^3\text{O}_2$. To explore the photochemistry of the various intermediates in the photooxidation of dimesityldiazomethane **3a**, irradiations in an 1 % oxygen doped argon matrix were investigated. Photolysis of **3a** with $\lambda > 435$ nm produces carbene **4a**. Annealing the O_2 -doped matrix for several minutes at 35 K results in the formation of dimesityl ketone oxide **5a**. Further irradiation with $\lambda > 515$ nm leads to dimesityldioxirane **6a**, which rearranges by photolysis with $\lambda > 435$ nm to mesityl mesitoate **9a**. For preparative scale synthesis of dioxirane **6a** a special designed photoreactor (Figure 3) was developed using a Hg/Cd arc lamp and a CuCl_2/HCl filter solution ($\lambda > 400$ nm and 50 % transmission at 435 nm). The irradiation was carried out in CCl_3F purged with oxygen at -78°C . By adding dimesityldiazomethane in several small portions to the photolysis mixture higher yields (up to 300 mg of **6a**, 50 - 60 % in the crude mixture) were obtained. After 10 - 12 hours of irradiation most of the diazo compound **3a** is consumed. At higher concentration of **3a** substantial amounts of ketone **7a** is formed. Dioxirane **6a** is purified after evaporation of the solvent by preparative scale HPLC chromatography and recrystallized from pentane to give colorless crystals. The half lifetime of **6a** in CDCl_3 at room temperature is about one day¹¹. Diazo compound **3b** was irradiated under the same conditions and the photolysis mixture investigated by analytical HPLC. Three new signals in the chromatogram were obtained. The products have not yet been identified. Compared to the mesityl systems these signals presumably belong to ketone, ester and dioxirane.



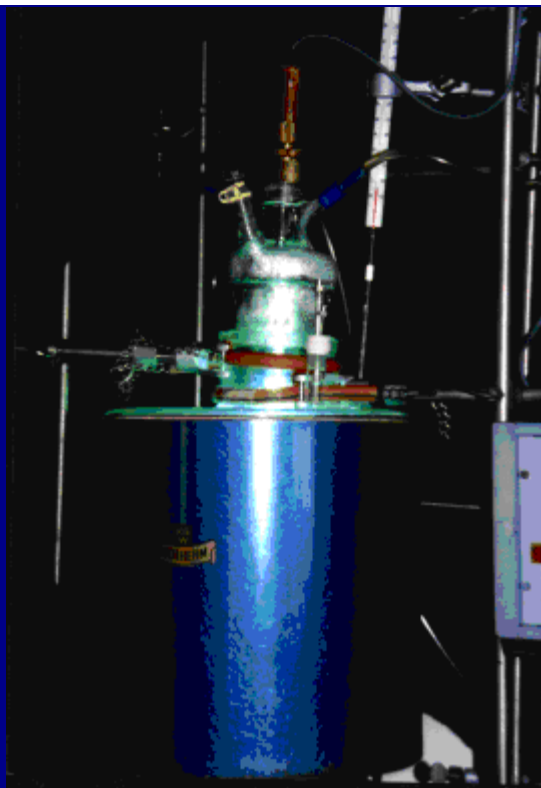


Figure 3: Photoreactor for the preparative scale synthesis of stable dioxiranes.

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5. Spectroscopic Characterization of Dimesityldioxirane

NMR spectra were obtained at -40°C . In $^1\text{H-NMR}$ the three signals at 2.19 (s, 12 H), 2.24 (s, 12 H), and 6.82 (s, 4H) were assigned to the o-methyl, p-methyl and m-aromatic protons of the mesityl rings. The $^{13}\text{C-NMR}$ spectrum shows $\delta = 103.0$ ppm for the quaternary carbon atom. By a H-C long-range correlation spectra the other six signals found at $\delta = 20.9$ and 21.6 ppm were assigned to p-methyl and o-methyl groups. The aromatic carbon atoms were observed at $\delta = 130.6$ (meta), 130.5 (ipso), 137.5 (ortho), and 139.0 (para) ppm ¹¹.

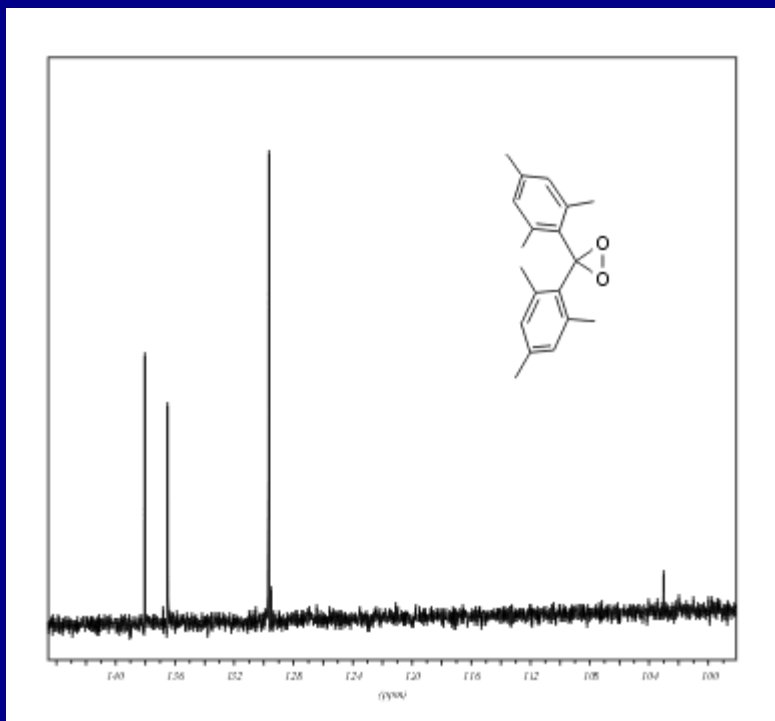


Figure 4: $^{13}\text{C-NMR}$ spectra of dimesityldioxirane **6a** at -40°C .

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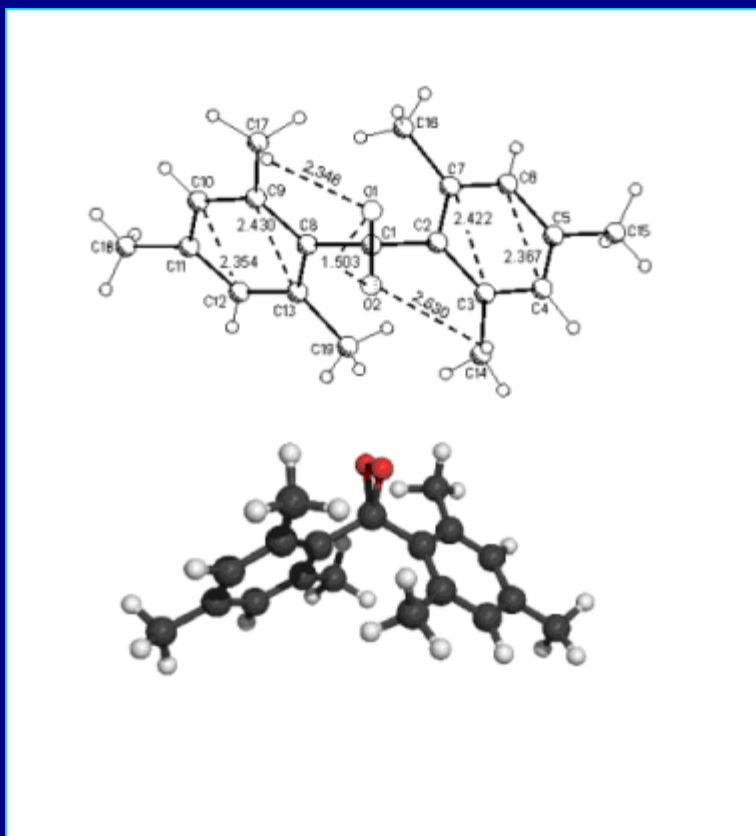
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6. X-ray Structure of Dimesityldioxirane

The X-ray structure of dimesityldioxirane **6a** reveals a comparatively short O-O distance of 1.503 Å, which is responsible for the stability of **6a** at room temperature (Figure 5). The C-O distance is about 1.414 Å. The steric repulsion of the mesityl groups leads to a widening of the C-C-C angle (119.2°), which results in a smaller O-C-O angle of 64.2°. The distance between the o-methyl hydrogen atom and the oxygen atom are 2.346 Å and 2.530 Å, respectively. B3LYP calculations with a 6/31G (d) basis set gives a C-O bond distance of 1.414 Å and a O-O bond distance of 1.490 Å¹¹. For the parent dioxirane the O-O bond distance was determined to 1.516 Å by microwave spectroscopy (Table 1).



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Figure 5: X-ray structure of dimesityldioxirane.

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- [1] Criegee, R.; Wenner, G. *Liebigs Ann. Chem.* 1949, 564, 9-15.
- [2] Criegee, R. *Angew. Chem.* 1975, 87, 765-771;
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7. Theoretical Investigations

Based on DFT methods the carbonyl O-oxide structures of **5a** and **5b** were calculated (Figure 6). The nonbonding O...H distance between the terminal COO oxygen atom and a neighboring hydrogen atom is shortened from 2.093 Å in **5a** to 2.050 Å in **5b**. This interaction demonstrates the high polarity of the COO group and leads to a stabilization of the carbonyl oxide. To achieve a close interaction between the terminal oxygen atom and one of the o-methyl or phenyl hydrogen atoms the out of the COO plane twisting of the mesityl ring in **5a** and the phenyl ring in **5b** is 57.3° and 9.5° respectively.¹⁸

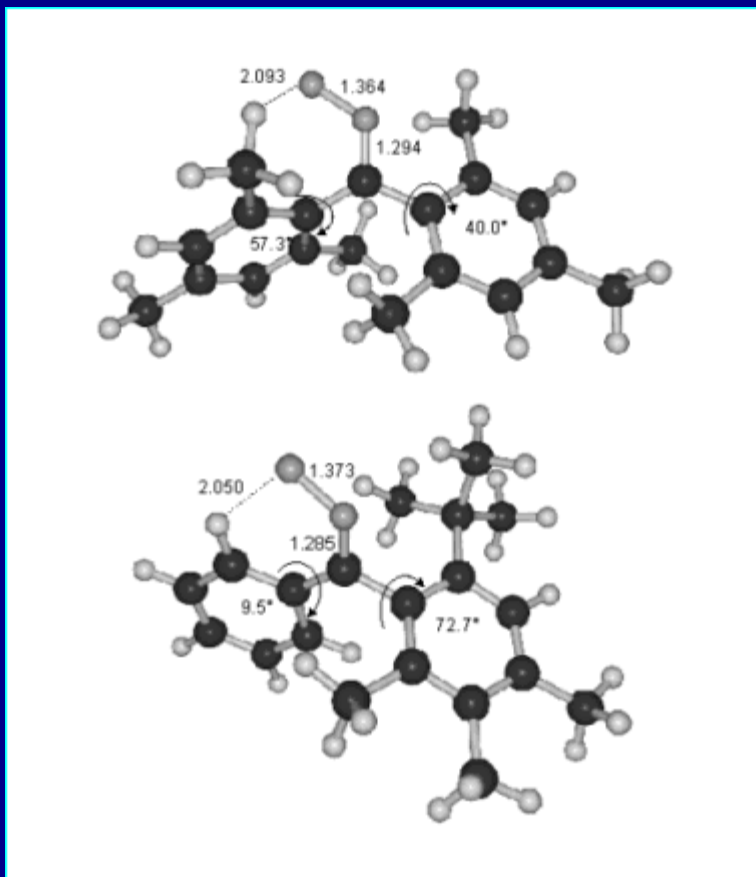


Figure 6: Calculated structures of Dimesitylcarbonyl-O-oxid **5a** and (6-*t*-Butyl-2,3,4-trimethylphenyl)phenylcarbonyl-O-oxid **5b**.

The B3LYP/6-31G* calculation of dioxirane **6b** leads to a O-O distance of 1.494 Å and a C-O distance of 1.414 Å (Figure 7). The OCO angle is with 63.77° and the RCR angle with 119.38° comparable to **6a** (Table 1). The nonbonding distance between ortho-methyl hydrogen and dioxirane oxygen is with 2.3638 Å similar to that of **6a**, while the distance of the *t*-butyl hydrogen and the oxygen is shortened to 2.2060 Å.

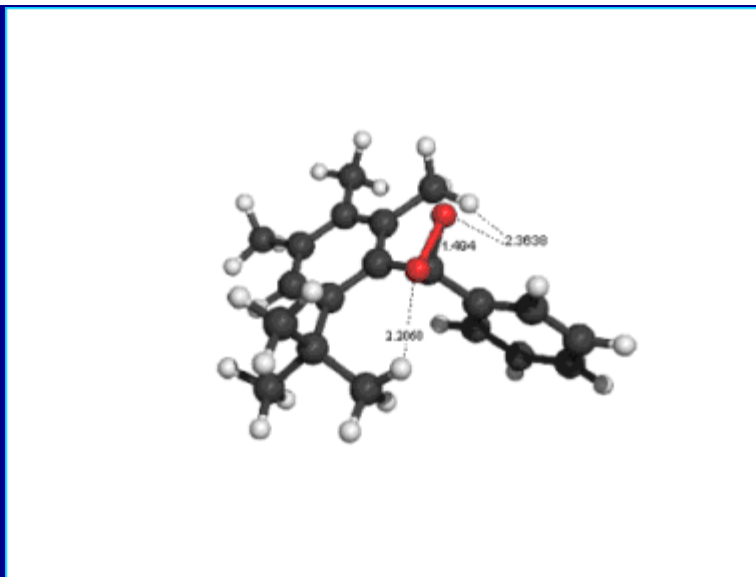
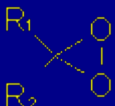


Figure 7: Calculated structure of (6-*t*-Butyl-2,3,4-trimethylphenyl)-phenyldioxirane **6b**.

Table 1: Structural Parameters of Dioxiranes

		Method	r (O-O) [Å]	r (C-O) [Å]	q (OCO) [°]	q (RCR) [°]
	R ₁ = R ₂ = H ^a	Microwave	1.516(3)	1.388(4)	66.2(2)	117.3(2)
	R ₁ = R ₂ = H ^b	CCSD(T)	1.514	1.385	66.2	116.6
	R ₁ = R ₂ = F ^c	High-res. IR	1.576	1.349	71.5	109.05
	R ₁ = R ₂ = F ^d	CCSD(T)	1.569	1.343	71.5	108.8
	R ₁ = R ₂ = CH ₃ ^d	MP2/6-31G(d)	1.521	1.417		121.3
5a	R ₁ = R ₂ = Mesityl ^f	X-Ray structure	1.503(5)	1.414(4) ⁹	64.2(3)	119.2(4)
5a	R ₁ = R ₂ = Mesityl ^f	B3LYP/6-31G(d)	1.490	1.414		120.5
5b	R ₁ = 2,3,4-trimethyl-6- <i>t</i> -butyl R ₂ = Phenyl	B3LYP/6-31G(d)	1.494	1.410 1.418	63.77	119.28

a: Ref. ¹³.

b: Ab initio calculation at the CCSD(T)(full)/cc-VTZ2P+f,d level, Ref. ¹⁴.

c: Ref. ¹⁵, best estimate with the C-F bond length constrained to 1.315 Å.

d: Ref. ¹⁶.

e: Ref. ¹⁷.

f: Ref. ¹¹.

⁹: Mean value of 1.413(5) and 1.414(5) Å.

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