Dimesityldioxirane

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Abstract: The preparative scale synthesis of dimesityldioxirane (**5**) via oxidation of dimesitylcarbene (**6**) is described. The dioxirane was obtained as colorless crystalline material, completely stable at −20 °C and characterized by spectroscopic methods, X-ray crystallography, and DFT calculations (B3LYP/6-31G(d)). The molecule shows approximately local C_2 symmetry with the mesityl rings twisted by ca. 60°. The experimental structural parameters, e.g., the O−O distance of 1.503 Å, are in good agreement with the theoretical values. The relief of steric strain caused by the mesityl groups is discussed in terms of the geometric distortion of the three-membered ring and the mesityl groups. Conformational features of **5** in solution are nicely reflected by measured and calculated (SOS-DFPT) NMR chemical shifts.

Introduction

During the last decade derivatives of dioxirane (**1**) have evolved from laboratory curiosities, stable only at low temperature,[1−4] to versatile oxygen transfer reagents.[5−10] A number of dioxiranes were characterized by IR spectroscopy in cryogenic matrices.[1,3] Dimethyldioxirane (**2**),[11,12] methyl-(trifluoromethyl)dioxirane (**3**),[13] and several alkyl-substituted dioxiranes[11] were prepared by the Caroate route and are fairly stable in dilute solution. **2** and **3** are now frequently used in preparative oxidations. Suenram and Lovas synthesized the highly labile parent dioxirane (**1**) via the ozonolysis of ethene at low temperature and determined the structure by microwave spectroscopy.[14] The O−O bond length is 1.516 Å (Table 1), which is significantly longer than r(O−O) in H_2O_2 with 1.49 Å[15,16] and other peroxides (1.44−1.50 Å),[17] but in the range of r(O−O) in dioxetanes (1.49−1.55 Å).[17,18] The calculation of reliable structural parameters of **1** requires the inclusion of correlation effects (at least MP2 theory)[19,20] and the use of large basis sets. At the CCSD(T) level of theory an almost quantitative agreement of theory and experiment was found (Table 1).[20,21]

The only other dioxirane for which experimental structural data are reported is difluorodioxirane (**4**), which is stable in the gas phase at room temperature.[22] High-resolution IR spectroscopy yields an O−O bond distance of 1.576 Å,[23] and a recent value determined by electron diffraction is 1.578 Å (Table 1).[24] Thus, fluorine substitution results in a significant lengthening of r(O−O), in agreement with theoretical predictions.[24−27]

1 R = R' = H
2 R = R' = CH_3
3 R = CH_3, R' = CF_3
4 R = R' = F
5 R = R' = Mes

A general route to dioxiranes is the oxidation of triplet carbenes with molecular oxygen $^3O_2$.[3] Singlet carbenes are also

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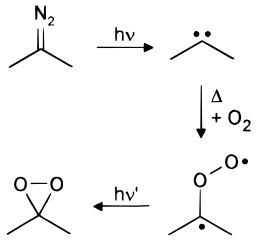
Table 1. Structural Parameters of Dioxiranes

	method	r(O−O)	r(C−O)	θ_{OCO}	θ_{RCR}
1 R = H[a]	microwave	1.516(3)	1.388(4)	66.2(2)	117.3(2)
R = H[b]	CCSD(T)	1.514	1.385	66.2	116.6
4 R = F[c]	high-resolution IR	1.576	1.349	71.5	109.05
R = F[d]	electron diffraction	1.578(1)	1.348(8)	71.7(5)	108.8(7)
R = F[d]	MP2/6-311G(2d)	1.576	1.349	71.5	108.8
R = F[e]	CCSD(T)	1.569	1.343	71.5	108.8
2 R = CH_3[f]	MP2/6-31G(d)	1.521	1.417		121.3
5 R = mesityl[g]	X-ray structure	1.503(5)	1.414(4)[h]	64.2(3)	119.2(4)
R = mesityl[g]	B3LYP/6-31G(d)	1.490	1.414		120.5

[a] Reference 14. [b] Ab initio calculation at the CCSD(T)(full)/cc-VTZ2P+f,d level, ref 21; see also ref 20. [c] Reference 23, best estimate with the C−F bond length constrained to 1.315 Å. [d] Reference 24. [e] Reference 27. [f] References 12 and 50. [g] This work. [h] Mean value of 1.413(5) and 1.414(5) Å.

oxidized; however, the reactivity is several orders of magnitude lower.[28,29] The primary products of these reactions are carbonyl *O*-oxides, which on irradiation with visible light readily rearrange to the dioxiranes. Several problems have to be solved to utilize this procedure for a preparative scale synthesis: (i) Carbenes are highly reactive, and thus the oxidation has to compete with other inter- and intramolecular reactions. (ii) The cyclization of carbonyl oxides to dioxiranes is a photochemical reaction,[3] and thus a long lifetime of the carbonyl oxide is necessary to obtain high yields of dioxiranes. (iii) Dioxiranes rearrange to esters on 400 nm irradiation. The photochemical dediazoniation of the diazo compound and the cyclization of the carbonyl oxide must occur at wavelengths at which the dioxirane is stable. The ideal conditions are thus an inert solvent with high O_2 solubility at low temperature, a diazo compound with long-wavelength absorption maxima, and a carbene which is comparatively long-living in solution.



A carbene that meets these requirements is dimesitylcarbene (**6**), which is easily generated by irradiation of dimesityldiazomethane (**7**). UV−vis and ESR spectra of carbene **6** in organic matrices at 77 K and kinetic data in solution from laser flash photolysis (LFP) experiments were reported by several authors.[30−32] In organic glasses at 77 K carbene **6** is stable for hours, and in cyclopentane or benzene at room temperature the lifetime is still ca. 200 μs,[30] compared to only 1.7 μs for diphenylcarbene.

Scaiano et al. were able to generate dimesityl *O*-oxide (**8**) as a transient with λ_{max} = 390 nm by laser flash photolysis of **7** in O_2-purged solvents.[31] The reaction rate of **6** with O_2 was determined to be 1.3×10^8 M^{-1} s^{-1} (in benzene), only one order of magnitude slower than the reaction of diphenylcarbene with O_2.[31] Therefore, in the presence of oxygen **6** is efficiently trapped to carbonyl oxide **8**. The lifetime of **8** is several orders of magnitude longer than that of benzophenone *O*-oxide.[31] In contrast to other diaryl carbonyl oxides, for which a second-order decay was found, the steric hindrance in **8** causes first-order decay.

These properties make the system dimesityldiazomethane/O_2 ideally suited for the preparative scale synthesis of the sterically highly congested dimesityldioxirane (**5**).[33] Here we report on the synthesis, spectroscopic properties, and structural characterization of the first crystalline dioxirane.

Results and Discussion

Synthesis in Argon Matrices. To explore the photochemistry and spectroscopic properties of the various intermediates in the photooxidation of **7**, matrix isolation experiments were carried out. Irradiation (λ > 435 nm, 10 K) of **7** in solid argon doped with 1% O_2 produces carbene **6** and small amounts of oxidation products of the carbene. In the UV spectrum the carbene exhibits an absorption maximum at 274 nm with a structured tailing to the red. The reported absorption with λ_{max} = 330 nm in organic glasses[30] presumably is a shoulder of the 274 nm band. In the IR strong absorptions at 2977 (ν_{CH}), 1487, 1460, and 854 cm^{-1} are assigned to **6**.

Annealing the O_2-doped matrix for several minutes at 35 K results in a yellow coloring of the matrix and formation of a new absorption with λ_{max} = 394 nm, which is assigned to dimesityl ketone *O*-oxide (**8**). All IR vibrations of **6** decrease in intensity, and new absorptions of **8** at 1612 (83), 1451 (46), 1430 (100), 1358 (21), 984 (21), 877 (33), 850 (50), and 539 (17) cm^{-1} (rel. intens.) are grow in. With $^{18}O_2$ only two absorptions show a significant isotopic shift: the band at 877 cm^{-1} is shifted to 846 cm^{-1} and assigned to the O−O stretching vibration. The frequency and the large isotopic shift are highly characteristic for the O−O stretching vibration in carbonyl oxides. The band at 1358 cm^{-1} is shifted to 1347 cm^{-1}, which indicates some contribution of C−O stretching.

Carbonyl oxide **8** is highly photolabile, and irradiation with λ > 515 nm rapidly yields dimesityldioxirane (**5**) (Scheme 1, Figure 1a). The dioxirane exhibits IR absorptions at 1457 (85), 1443 (31), 1423 (85), 1289 (100), 1096 (23), 973 (31), 887 (69), 733 (15), and 513 (23) cm^{-1} (rel. intens.). The only vibration for which an ^{18}O-isotopic shift is clearly observed is the 1096 cm^{-1} vibration (shifted to 1090 cm^{-1}). Shorter wavelength irradiation produces mesityl mesitoate (**9**) as the only detectable product (Figure 1b), while dimesityl ketone (**10**) is not formed during any of the photolysis steps. Both **9** and **10** were independently synthesized and matrix isolated to prove the identity of the oxidation products of **6**.

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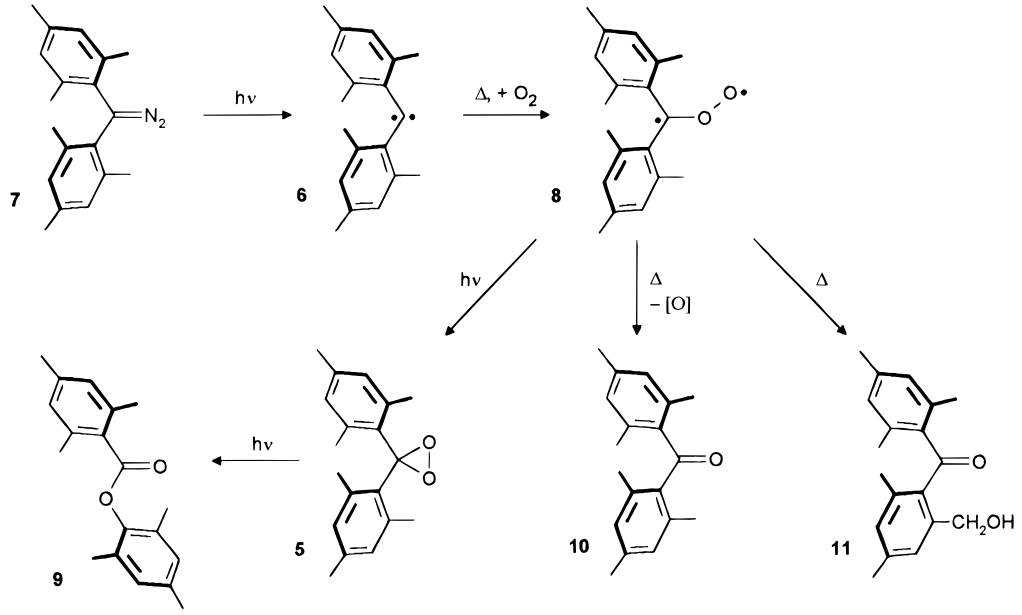
Scheme 1



These experiments clearly demonstrate that the photooxidation of diazo compound **7** produces high yields of dioxirane **5** if the reaction conditions are carefully chosen. Principally this reaction should allow for a preparative scale synthesis of **5**.

Synthesis in Organic Glasses. Diazomethane **7** (1.5×10^{-3} M) is dissolved in an oxygen-saturated (1 bar of O_2, −20 °C) mixture of $CFCl_3$ and $(CF_2Br)_2$ (1:1),[34] and cooled to 77 K to produce a transparent glass. Irradiation with $\lambda > 515$ nm results in an intense yellow coloring of the glass, caused by the broad and intense absorption of carbonyl oxide **8** at $\lambda_{max} = 398$ nm. Melting the glass at 160 K results in a yellow solution of **8** which is stable at 195 K (−78 °C) in the dark for several hours. In these solutions **8** was unequivocally characterized by ^{13}C- and ^{1}H-NMR spectroscopy.[34] Exposure to daylight or irradiation with $\lambda > 455$ nm rapidly causes the complete bleaching of the glass or solution. If a glass after bleaching the carbonyl oxide is slowly warmed to the melting point (160 K), some carbonyl oxide is formed back, indicating the presence of unreacted carbene even in oxygen-saturated glasses at 77 K.

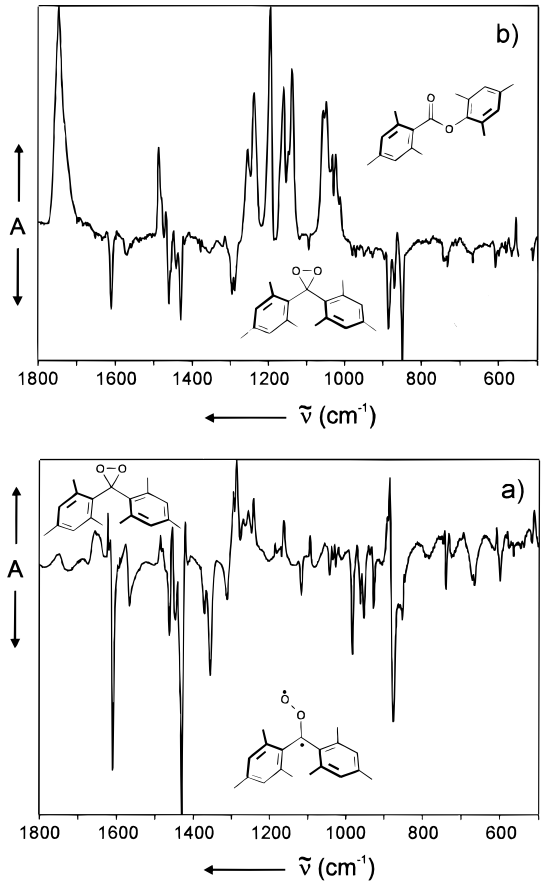


Figure 1. Difference IR spectra showing the photochemical reaction sequence **8** → **5** → **9** in argon at 10 K. (a) Bottom: bands of carbonyl oxide **8** disappearing on $\lambda > 515$ nm irradiation. Top: bands of dioxirane **5** appearing. (b) Bottom: bands of dioxirane **5** disappearing on $\lambda > 420$ nm irradiation. Top: bands of ester **9** appearing.

After being warmed to room temperature, the stable products were separated by HPLC (reversed phase/methanol−water) and characterized by conventional spectroscopic methods and independent synthesis. The major products are unreacted diazomethane **7**, ketone **10**, ester **9**, and dioxirane **5**. Minor products are dimesitylmethane (traces from a contamination of starting material **7**) and 2-(hydroxymethyl)-4,6-dimethylphenyl mesityl ketone (**11**). If the reaction mixture is irradiated with $\lambda > 420$ nm prior to the HPLC separation, the dioxirane peak decreases in intensity and more ester **9** is formed. These results confirm the photochemistry observed in solid argon. The ketones **10** and **11**, which are not formed in solid argon, are thermal products of carbonyl oxide **8**. Intermolecular oxygen transfer results in the formation of **10**, while intramolecular oxygen transfer produces **11**. The ester **9** is solely the photoproduct of dioxirane **5** and neither thermally nor photochemically formed from **8**.

Synthesis in Solution. For the preparative scale synthesis of **5** the use of inert gas matrices or organic glasses is impractical, and we thus investigated the photooxidation of **7** in solution. Initial experiments were carried out in a cooled 10 mL cuvette at −90 °C irradiated with a high-pressure mercury arc lamp and cutoff filters ($\lambda > 475$ and 495 nm). $CFCl_3$, $(CF_2Br)_2$, pentane, isopentane, and *n*-heptane were used as solvents. With 495 nm irradiation the yield of **5** is 40−50%, and the major byproducts are ketone **10** (30−35%), ester **9** (10−20%), and unreacted diazomethane **5**. In isopentane, the yield

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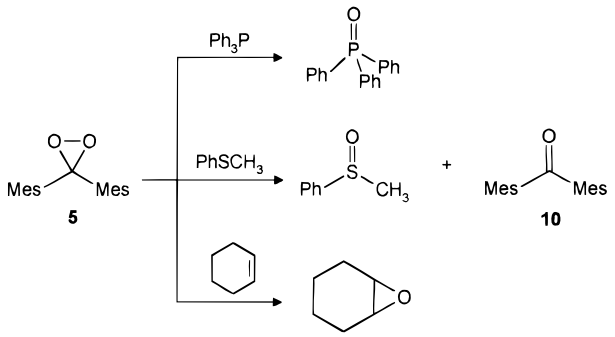
Scheme 2



of **5** is significantly lower and larger amounts of **10** are formed, indicating the oxidation of the solvent. Shorter wavelength irradiation (λ > 475 nm) in $CFCl_3$ reduced the time required for the complete consumption of **7** drastically; however, the yield of **5** dropped to 30%, and both the yields of **10** and **9** increased.

A special photoreactor was constructed that allowed up to 500 mg of **7** in 300 mL of O_2-purged $CFCl_3$ at −78 °C to be irradiated with the filtered light ($CuCl_2$/HCl filter with 50% transmission at 435 nm) of a Hg/Cd medium-pressure lamp. Due to the fire hazard of O_2-saturated hydrocarbon solutions, only $CFCl_3$ was used in the preparative scale syntheses of **5**. After 10 h of irradiation most of the diazo compound **7** is consumed. The highest yield of **5** (>50%) is obtained if the concentration of **7** is kept low by adding it in several small portions to the photolysis mixture. At higher concentration of **7** substantial amounts of ketone **10** are formed, indicating the oxidation of **7** by carbonyl oxide **8** (**7** is not oxidized by **5**). Dioxirane **5** is purified after evaporation of the solvent by preparative scale HPLC and recrystallized from pentane to give colorless crystals.

Solutions of pure **5** or the crystalline material can be stored in the dark at −20 °C for many months without decomposition, while crude photolysis mixtures are less stable. At room temperature crystalline **5** slowly (14% loss within two weeks) decomposes to an approximately 1:2 mixture of ester **9** and ketone **10**. The melting point is 62−64 °C with partial decomposition. The half-life of **5** in $CDCl_3$ at room temperature is on the order of one day, and the major product detected by ^{1}H-NMR spectroscopy is ester **9**, while only traces of **10** are formed. The stability of **5** in halogenated solvents such as CCl_4 or $CFCl_3$ is similar, while in methanol within several hours considerable amounts of both ester **9** and ketone **10** are formed. This indicates that methanol is slowly oxidized by dioxirane **5**. The photolysis (λ > 360 nm) of purified solutions of **5** quantitatively produces ester **9**, in agreement with the results from the matrix studies.

Dioxirane **5** is a powerful oxygen transfer reagent. Addition of **5** in $CDCl_3$ to equimolar amounts of triphenylphosphine (in CCl_4), phenyl methyl sulfide, or cyclohexene in the same solvent results within several minutes in the quantitative consumption of **5** and formation of the expected oxidation products (Scheme 2).

Spectroscopic Characterization. The UV spectrum of **5** in methanol exhibits a very strong absorption at λ_{max} = 206 nm (log ϵ = 4.6) and a strong absorption at λ_{max} = 274 nm (log ϵ = 3.2). Alkyldioxiranes form pale yellow solutions, caused by weak n−π* transitions around 320−350 nm extending to the red.[6] In contrast to this, crystals of **5** are completely colorless, and even in 10^{-2} M solutions of **5** a transition in the near UV or blue range of the spectrum could not be unequivocally detected, although the photochemistry of **5** on irradiation with blue light requires some absorption in this range.

IR spectra of **5** were recorded in solid argon, KBr, and CCl_4 solution. The absence of any absorption in the carbonyl range proves the purity of **5**. The IR spectrum of **5** is dominated by the mesityl groups, and the only absorption that shows a significant ^{18}O-isotopic shift is found at 1096 cm^{-1}. Presumably this isotopic shift is caused by some contribution of the C−O vibration to this mode. The O−O vibration of dioxiranes is expected in the range 730−800 cm^{-1},[21] and a weak absorption at 733 cm^{-1} that shows a small ^{18}O-isotopic shift might be attributed to this vibration.

The ^{1}H-NMR spectrum of **5** in $CDCl_3$ shows three signals at δ = 2.19 (s, 12 H), 2.24 (s, 6 H), and 6.82 (s, 4 H) assigned to the *o*-methyl, *p*-methyl, and *m*-aromatic protons of the mesityl rings, respectively. These signals are not broadened on lowering the temperature to −40 °C, which indicates that the two C_2 symmetric conformers are rapidly equilibrating by hindered rotation or libration of the mesityl groups.

The seven signals in the ^{13}C-NMR spectrum of **5** could be assigned by recording a DEPT spectrum, by specific ^{13}C-labeling of the three-membered ring, and by H−C long-range correlation. The signal of the four *o*-methyl groups is found at δ = 21.6 and that of the two *p*-methyl groups at δ = 20.9. The secondary aromatic carbon atom (meta position) is observed at δ = 130.6, and the three quarternary carbon atoms are observed at δ = 130.5 (ipso), 137.5 (ortho), and 139.0 (para). ^{13}C-labeling (99% ^{13}C) of the dioxirane carbon atom C(1) dramatically increases the intensity of the quarternary carbon atom at δ = 103.0, and thus unequivocally allows this signal to be assigned. The chemical shift of C(1) is in excellent agreement with the chemical shifts found in other dioxiranes such as dimethyldioxirane (**2**, δ = 102.3),[12,35,36] methyl(trifluoromethyl)dioxirane (**3**, δ = 97.3),[37] or ethylmethyldioxirane (δ = 103.9).[7]

The experimental NMR spectrum is nicely reproduced by the calculated (SOS-DFPT)[38,39] chemical shifts (Figure 2a). The calculation allows the NMR chemical shifts of a fixed conformation of **5**, which is experimentally not accessible, and of the ^{17}O nuclei to be discussed. The calculated ^{17}O shift agrees well with known and calculated shift values of other dioxiranes. Compared to the ^{17}O chemical shift of dimethyldioxirane (δ(^{17}O) = (exp) 338, (calcd) 334 ppm),[40] the ^{17}O nuclei in **5** (δ(^{17}O) = 321 ppm) are somewhat more shielded. While the protons of the *p*-methyl and the C(14) and C(17) *o*-methyl groups possess typical values found also for toluene (two more deshielded protons, one more shielded proton), the ^{1}H shifts of the C(16) and C(19) *o*-methyl groups suggest that two protons rather than one are shielded (Figure 2). This is a result of methyl group rotation, which places one H atom above the benzene ring in the shielding region of the ring current.

Structural Characterization. In the crystal (Figure 3a) dioxirane **5** possesses approximately local C_2 symmetry with the two mesityl groups twisted by 61.6° and 53.7° from the C(2)−C(1)−C(8) plane, respectively. B3LYP[41−43] calculations

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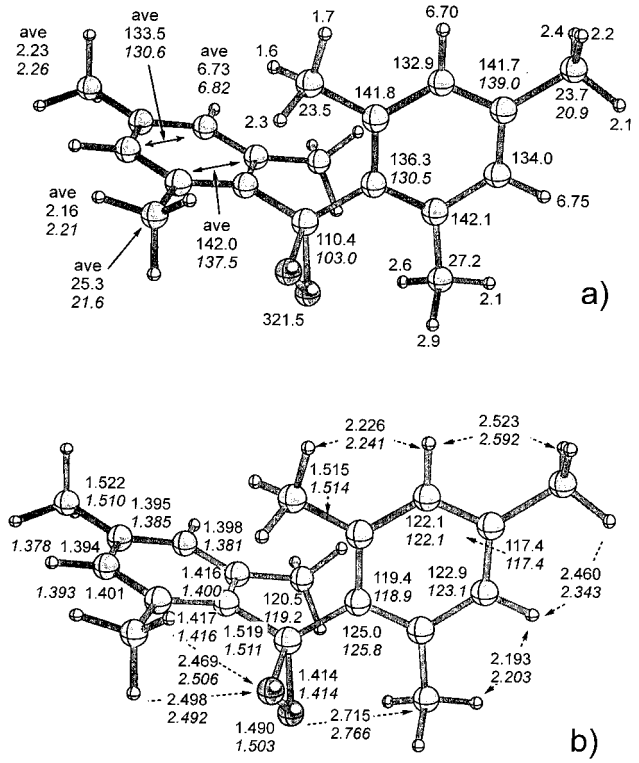

Figure 2. BPW91/VTZ+P SOS-DFT calculated NMR and structural data of dimesityldioxirane (**5**) compared to experimental values. (a) SOS-DFPT NMR chemical shifts (ppm) relative to TMS (^{1}H and ^{13}C) and gaseous H_2O (^{17}O) for **5**. For methyl groups and C atoms that are equilibrated by hindered rotation, average values (ave) are compared with the corresponding experimental values (in italics). (b) B3LYP/6-31G(d) geometry of **5** compared to the crystal structure. Since the calculated C_2 symmetrical structure is slightly distorted in the crystal (see Figure 3b), the experimental values given here (in italics) are averaged values over corresponding bond lengths and angles in the two mesityl rings.

with a 6-31G(d) basis set[44] lead to C_2 symmetry and a twisting of the mesityl groups by 54.2° in reasonable agreement with the crystal structure (Figure 2b), where one has to consider that packing forces in the unit cell probably lead to deviations from C_2 symmetry and somewhat different twist angles. Steric strain caused by the mesityl groups is relieved in different ways (Figures 2b and 3b): (a) Rotation of the mesityl groups. (b) The central C(2)−C(1)−C(8) angle is widened to 119.2° (B3LYP 120.5°), which is clearly larger than the corresponding value for dioxirane (**1**; 117°, Table 1)[20,21] or difluorodioxirane (**4**; 109°).[27] (c) The *o*-methyl groups are slightly bent backward away from the dioxirane ring (widening of the C(17)−C(9)−C(8) angle to 126°). (d) The benzene hexagon is distorted in a way that the distances C(9)−C(13) (2.430 Å, B3LYP 2.446 Å) and C(3)−C(7) (2.422 Å) are larger than the distances C(10)−C(12) (2.354 Å, B3LYP 2.383 Å) and C(4)−C(6) (2.367 Å), respectively. (e) The *o*-methyl groups are rotated by 20.2° and 22.6° (averaged B3LYP values) relative to the methyl group in toluene (*p*-methyl rotation 3.8°) so that steric interactions between the mesityl groups and the dioxirane ring become smaller. As a result of (a)−(e), there are no close contacts in **5** and all H−H and O−H distances are within the region of typical van der Waals values.

Compared to that in the parent compound **1**, *r*(O−O) in **5** (exp, 1.503 Å; B3LYP, 1.490 Å; Table 1, Figure 3) is shortened by 0.013 Å while the CO bonds are slightly longer (exp, 1.414; B3LYP, 1.414; **1**, exp, 1.388 Å; Table 1). Obviously, a widening of the central C2−C1−C8 angle implies a decrease of the OCO angle and a shortening of the OO bond. In MO terms, the widening of the external ring angle leads to a stabilization of orbital $\pi 2$ of the ring, which is OO bonding and CO antibonding. This is in line with a larger negative charge at the O atoms (the dioxirane ring accepts 0.151 e from the two mesityl groups) and a stronger shielding of the O nuclei (see above). Since the strength of the OO bond determines the reactivity of a dioxirane, which is characterized by OO bond rupture, formation of a methylenebis(oxy) biradical, and subsequent rearrangements and decompositions of this biradical, **5** should be more stable than other dioxiranes.

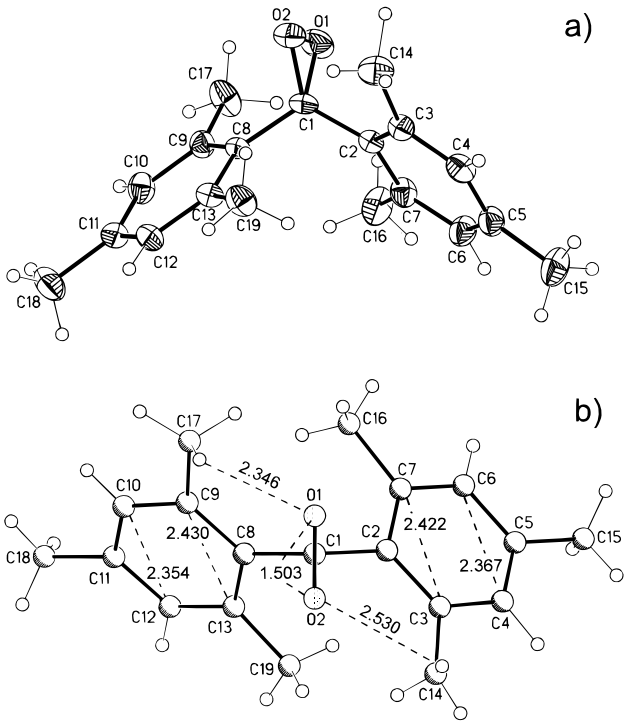

Figure 3. X-ray crystal structure of dimesityldioxirane (**5**).

Dioxiranes are in general about 20 kcal/mol (**1**, 25.6; R = H, R = CH_3, 21.0;[45] **2**, 19.8[46]), in the case of difluorodioxirane (**4**) even 42.3 kcal/mol,[27] more stable than the corresponding carbonyl oxides. In **5** the energy difference between the two isomers is just 9.9 kcal/mol, indicating that dimesityl ketone oxide is strongly stabilized relative to **5**.[40] There seems to be no particular increase in the thermodynamic stability of the dioxirane ring of **5** due to the mesityl groups, which can be understood in view of the twisting of the mesityl groups. The twisting angle of about 55° prevents strong interactions of the phenyl ring MOs with either the Walsh or the π-MOs of the dioxirane ring. On the other hand, steric repulsion between the mesityl rings guarantees the kinetic stability of **5** since ring opening implies an increase in steric interactions.

Conclusion

The preparative scale synthesis of dimesityldioxirane (**5**) was optimized on the basis of preliminary matrix isolation studies. The results nicely demonstrate that matrix isolation not only is useful for the spectroscopic characterization of reactive intermediates but also is a powerful tool for the optimization of larger scale syntheses. By carefully controlling the reaction conditions—expecially the light source and filters—more than 50% yield of **5** based on consumed dimesityldiazomethane (**7**) was obtained.

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(46) Gutbrod, R.; Schindler, R. N.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1996**, *252*, 221.

Dioxirane **5** is a sterically highly congested dioxirane that is completely stable at −20 °C and even at room temperature, as crystalline material decomposes only slowly. The stabilization of **5** compared to other dioxiranes is a kinetic effect caused by the steric shielding of C(1) and a thermodynamic effect related to the short OO bond distance. The major route of the thermal or photochemical decomposition is rearrangement to ester **9**. This rearrangement proceeds via cleavage of the OO bond and [1,2]-migration of a mesityl group in the methylenebis(oxy) biradical. The OO distance in **5** is the shortest of all known dioxiranes, and the OO bond is comparatively strong, which explains the high thermal stability of **5**. However, the oxygen atoms are still accessible in bimolecular reactions, and thus oxygen transfer to double bonds or hetero atoms is fast and highly efficient. We are currently investigating the chemistry of **5** to further explore the relation of structure and reactivity in dioxiranes.

Experimental Section

Materials and General Methods. ^{1}H and ^{13}C NMR were recorded with a Bruker AM 400 at 400.1 and 100.6 MHz, respectively, in $CDCl_3$ as solvent. IR spectra were obtained with a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 cm^{-1} in the range from 400 to 4000 cm^{-1}. UV spectra were taken on a Hewlett-Packard 8452A diode array spectrophotometer with a resolution of 2 nm. Preparative scale HPLC was carried out with a Knauer photometer (detection at λ = 254 nm), a Knauer HPLC pump 64, a Polygosil 60-10 CN column (250 mm), and ether/pentane as eluent at −20 °C with a flow rate of 9.5 mL min^{-1}. Analytical HPLC was carried out with a Merck-Hitachi diode array detector L-4500, a Knauer HPLC pump 64, a RP-18 column (125 mm; particle size 5 μm) and methanol as eluent with a flow rate of 0.5 mL min^{-1}.

Irradiations were carried out using Osram HBO 500 W mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation of the lamps was absorbed by a 10 cm path of water and by a Schott KG1 filter. For broad-band irradiation Schott cutoff filters were used (50% transmission at the wavelength specified), and for narrow-band irradiation, interference filters in combination with dichroic mirrors and cutoff filters (420, 435, 455, 475, and 495 nm) were employed.

Dimesityl ketone (**10**)[47] and mesityl mesitoate (**9**)[48] were synthesized according to literature procedures. The procedure of Zimmermann and Paskowich was used to synthesize dimesityldiazomethane (**7**).[49] The synthesis of [^{13}C]**7** labeled at the diazo carbon atom started from K^{13}CN (99% ^{13}C, Isotec Inc.) via Cu^{13}CN and [^{13}C]mesitonitrile. [^{13}C]**7**: IR (KBr) $\tilde{\nu}$ = 2915 (w), 2045 (C═N_2, s), 1608 (w), 1478 (m), 1379 (w), 1011 (w), 883 (w), 852 (w) cm^{-1} (rel. intens.); ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 20.6 (CH_3), 20.9 (CH_3), 58.0 (^{13}C═N_2), 126.0, 129.7, 136.9, 137.1; HRMS calcd 279.181 654, found 279.181 800.

Matrix Spectroscopy. Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) at 30 K on top of a CsI (IR) or sapphire (UV−vis) window at a rate of approximately 0.15 mmol/min.

Organic Glasses. An Oxford instruments liquid nitrogen bath cryostat (DN1714) equipped with four quartz windows and a quartz cuvette (5 mL) was used for variable temperature experiments in the range 77−300 K. Experiments at 77 K were also conducted in a simple quartz cuvette and a quartz Dewar vessel with optical windows. In a typical experiment a 1.53×10^{-3} M solution of dimesityldiazomethane (**7**) in a 1:1 mixture of $CFCl_3$ and $(CF_2Br)_2$ was saturated with oxygen at −20 °C for 20 min and cooled to 77 K to form a transparent glass. After irradiation of the glass with λ > 475 nm for 3 h the reaction mixture was warmed to room temperature, and the solvent was removed under reduced pressure. The yield of **5** in the crude photolysis solution was 55%.

Synthesis of 5 in Solution. The small-scale synthesis of **5** was carried out at −80 °C in a 20 mL quartz cuvette equipped with a cooling jacket and a laboratory cryostat (irradiation with λ > 475 nm, (1−3) $\times$ 10^{-3} M **7** in $CFCl_3$, O_2-purged at −20 °C). For the preparative scale synthesis of **5** a specially designed photoreactor with a 150 W Hg/Cd medium-pressure arc lamp (Heraeus-Nobelight TQ 150 Z3) was used. Compared to a Hg arc lamp, the irradiation times were drastically reduced by using the Cd-enhanced lamp. The lamp with a water cooling jacket, a filter solution jacket (2 cm), and a vacuum jacket was immersed into a 500 mL flask cooled to dry ice temperature. A $CuCl_2 \cdot 2H_2O$/HCl filter solution gave the highest yields ($CuCl_2 \cdot 2H_2O$, 86.31 g; aqua dest, 600 mL; concentrated HCl, 60 mL; 50% transmission at 435 nm). The flask was filled with 300 mL of $CFCl_3$ and purged with O_2 for 10 min. A 500 mg sample of dimesityldiazomethane (**7**) was added in small portions during the irradiation time (10 h). After merely complete consumption of **7** the solvent was distilled off in vacuum into a trap cooled with liquid nitrogen while the photolysis mixture was kept between −50 and −30 °C. The photolysis process was observed with analytical HPLC (RP-18 column, methanol as eluent). The yield of **5** in the crude reaction mixture was 50−60%. **5** was purified by preparative scale HPLC (Polygosil 60-10 CN at −20 °C with ether/pentane (1:100) as eluent) and recrystallized from pentane to give colorless crystals.

5: mp 62−64 °C; UV (CH_3OH) λ_{max} [nm] 206 (log ϵ = 4.6), 274 (log ϵ = 3.2); IR (CCl_4) 2923 (m), 1612 (m), 1571 (w), 1456 (m), 1295 (w), 1242 (m), 881 (m), 852 (s) cm^{-1}; ^{1}H NMR (−40 °C) δ = 2.19 (s, 12H, *o*-CH_3), 2.24 (s, 6H, *p*-CH_3), 8.82 (s, 4H, aromatic) ppm; ^{13}C NMR (−30 °C) δ = 20.9 (*p*-CH_3), 21.6 (*o*-CH_3), 103.0 (quaternary C), 130.6 (*m*-C), 130.5 (ipso-C), 137.5 (*o*-C), 139.0 (*p*-C) ppm; MS (70 eV) *m/z* (%) 282 (M^+, 1), 267 (2), 251 (7), 236 (2), 164 (3), 147 (100), 119 (26), 91 (16), 77 (10); HRMS calcd 282.161 980, found 282.162 500.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, and anisotropic and isotropic displacement parameters and the package diagram of dimesityldioxirane (**5**) (7 pages). See any current masthead page for ordering and Internet access instructions.

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