# Dimesitylketone *O*-Oxide: First NMR Spectroscopic Characterization of a Carbonyl *O*-Oxide

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Carbonyl *O*-oxides **1** are important reactive intermediates in many oxidation processes. Since Criegee postulated these elusive species as the key intermediates in the alkene–ozone reaction,[1,2] many experiments were reported to provide evidence for the existence of **1**. While the intermediacy of **1** was clearly
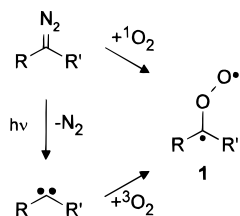
demonstrated by trapping experiments,[3] no successful attempt for the direct spectroscopic characterization of **1** in the ozonolysis reaction has been reported. However, the oxidation of triplet carbenes with $^3O_2$ (triplet route, spin allowed to yield singlet **1**) or diazo compounds with $^1O_2$ (singlet route) provides effective methods for the spectroscopic characterization of carbonyl oxides **1** in cryogenic matrices[4,5] (only the triplet route) or in solution using time-resolved spectroscopy[6,7] (singlet and triplet route).

Recently we reported on the generation (triplet route) and UV–vis spectroscopic characterization of dimesitylketone *O*-oxide **2** in Freon glasses and solution at low temperature.[8] We now describe the generation of **2** in solution by both the triplet and singlet route and the first ^1H- and ^{13}C-NMR spectrum of a carbonyl *O*-oxide.

Dimesityldiazomethane **4** was dissolved in a 1:1 mixture of CFCl$_3$ and (CF$_2$Br)$_2$, oxygen saturated at −10 °C, and cooled to 77 K to form a transparent glass. Irradiation (λ = 515 nm) into the absorption maximum of **4** (λ = 498 nm) produced a new species with an intense, broad absorption at 398 nm which has been assigned to carbonyl *O*-oxide **2**.[8] After melting the glass and warming the solution to −78 °C a yellow solution of **2** was obtained which was stable at this temperature in the dark for many hours. Upon irradiation with λ > 475 nm for several minutes the yellow color rapidly disappeared, and a mixture of dimesityldioxirane **5** and mesityl mesitoate **6** was formed.[8]

The experiment was also followed by NMR spectroscopy. In the ^1H-NMR spectrum of the yellow solution at −70 °C resonances at δ = 6.95 (1 H), 6.82 (2 H), 2.53 (3 H), 2.28 (3
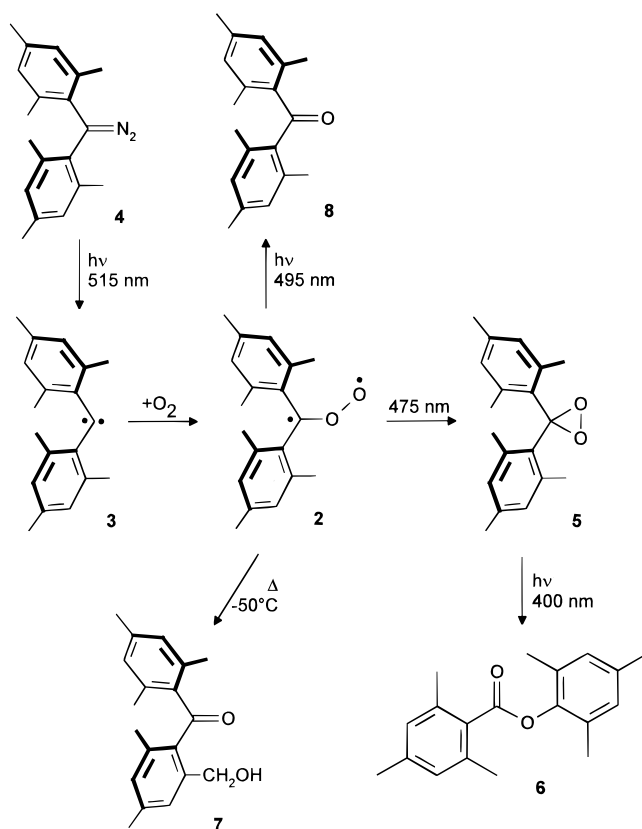
H), 2.25 (3 H), 2.05 (6 H), and 1.61 (3 H) rapidly disappeared on warming to room temperature or irradiation with visible light and were assigned to carbonyl oxide **2** (Figure 1). About 20–25% of the diazo precursor **4** was converted to **2**, less than 5% to dimesitylketone **8**. Other products were not detected in the NMR spectrum. One missing aromatic proton of **2** and the aromatic protons of ketone **8** are hidden under the intense and broad resonance of the remaining diazo precursor (δ = 6.72). There are five singlets observed for the six methyl groups; one, at δ = 2.05, corresponds to two methyl groups. The number of methyl groups observed clearly demonstrates that the rotation of the mesityl rings is frozen and the two mesityl rings are not equivalent. Thus the C–O–O moiety is configurationally stable
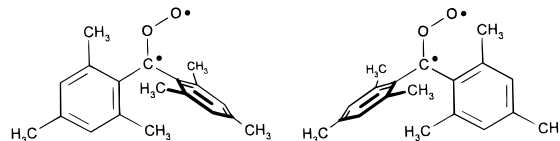
at −70 °C. Obviously two *m*-hydrogen atoms and two methyl groups are equivalent, which corresponds to a structure with one mesityl ring lying in the C–O–O plane and one perpendicular to it.

If a ^{13}C-labeled sample of diazomethane **4** (99% ^{13}C at the diazo carbon atom) was irradiated under the same conditions as described above, a new ^{13}C resonance at a chemical shift δ = 211.1 was observed, which was assigned to the carbonyl carbon of **2**. Warming to room temperature resulted in the disappearance of **2** and the formation of **7** (δ = 204.7, main product)[9] and **8** (δ = 202.5) (Figure 2), while dioxirane **5** was not formed during the warmup. Cremer and Schindler calculated (using the IGLO method) the chemical shift for the parent carbonyl *O*-oxide H$_2$C–O–O to δ = 227,[10] and thus the assignment of the resonance at δ = 211.1 to carbonyl *O*-oxide **2** is in qualitative agreement with theory.

An alternative synthesis of carbonyl oxides is the reaction of diazo compounds with singlet oxygen.[6,7] A solution of dimesi-

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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; *Angew. Chem., Int. Ed. Engl.* **1975,** *14,* 745.
(3) Kuczkowski R. L. In *Ozone and Carbonyl Oxides*; Padwa A., Ed.; Wiley: London, 1984; Vol. 2, Chapter 11, p 197.
(4) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983,** 1213–1215.
(5) Sander, W. *Angew. Chem.* **1990,** *102,* 362–372; *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 344–354.
(6) Agarwal, S. K.; Murray, R. W. *Isr. J. Chem.* **1983,** *23,* 405–408.
(7) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem.* **1989,** *54,* 1612–1616.
(8) Kirschfeld, A.; Muthusamy, S.; Sander, W. *Angew. Chem.* **1994,** *106,* 2261–2263; *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 2212.
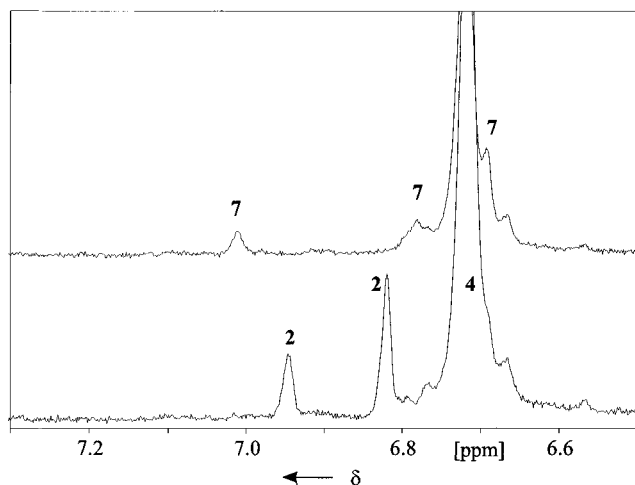
Figure 1. ^{1}H-NMR spectra showing the thermal reaction of **2** to produce **7** and **8**. Bottom: Spectrum produced by irradiation ($\lambda = 515$ nm) of **4** in O_2-saturated $CFCl_3/(CF_2Br)_2$ at 77 K and subsequent warming to -70 °C. Top: Same as A, but additional warming to room temperature and recooling to -70 °C.

Figure 2. ^{13}C-NMR spectra showing the thermal reaction of **2** to produce **7** and **8**, same experiment as in Figure 1. Bottom: Spectrum produced by irradiation ($\lambda = 515$ nm) of [13]C-**4** in O_2-saturated $CFCl_3/(CF_2Br)_2$ at 77 K and subsequent warming to -70 °C. Top: Same as A, but additional warming to room temperature and recooling to -70 °C.

tyldiazomethane **4** (4×10^{-3} mol L^{-1}) and rose bengal B (3×10^{-5} mol L^{-1}) in dry THF was saturated with oxygen at room temperature. Irradiation of the solution with $\lambda > 570$ nm at -110 °C resulted in the formation of the intense absorption of **2** with $\lambda_{max} = 394$ nm. An isosbestic point at 470 nm suggested that **2** was the only product formed during the irradiation and allowed to calculate the extinction coefficient ($\epsilon = 4400$ L cm^{-1} mol^{-1}). In the absence of rose bengal B no reaction was observed under the same conditions. With $t = 30$ min at -70 °C in THF, compared to $t = 25$ min at -40 °C in $CCl_3F/(CF_2Br)_2$, carbonyl oxide **2** is significantly less stable in THF than in the Freon mixture. However, oxidation products of THF could not be detected, so far.

The synthesis of **2** by two independent routes confirms the assignment of the structure of a carbonyl *O*-oxide. The thermal reaction of **2** exclusively leads to ketones **7** and **8**, the products of the intra- and intermolecular oxygen transfer, but not to dioxirane **5**. Simple model calculations using PM3/UHF reveal a very short nonbonding distance of 1.85 Å between the terminal oxygen atom and one of the ortho methyl hydrogen atoms. Both the stepwise insertion with the intermediate formation of an oxygen atom and the concerted insertion are conceivable reaction mechanisms for the formation of **7**.[11]

Photolysis of **2** leads to **5** and ketone **8**, while ester **6** is the product of the secondary photolysis of **5**. These results are in excellent agreement with previous experiments in inert gas matrices.[4,5,12−18]

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(9) **7** was synthesized by warming a solution of **2** in Freon to room temperature and purified by HPLC separation: IR (KBr) $\nu = 3424$ (m, ν_{OH}), 2964 (vs), 2929 (m), 1651 (s, ν_{CO}), 1608 (s), 1430 (m), 710 (m) cm^{-1}; ^{1}H-NMR (400 MHz, CDCl$_3$) $\delta = 7.16$ (s, 1 H), 6.92 (s, 1 H), 6.86 (s, 2 H), 4.48 (d, J = 6.7 Hz, 2 H, C*H*$_2$OH) 2.35 (s, 3 H), 2.30 (s, 3 H), 2.09 (s, 6 H, o-CH$_3$), 1.90 (s, 3 H, CH$_3$); ^{13}C-NMR (100 MHz, CDCl$_3$) $\delta = 203.9$, 141.0, 140.5, 137.0, 136.3, 132.0, 129.9, 129.8 (CH), 65.3 (CH$_2$OH), 21.3 (CH$_3$), 21.2 (CH$_3$), 20.8 (CH$_3$), 20.7 (CH$_3$); HR-MS: calcd 282.1620, found 282.1619 ± 2 ppm.
(10) Cremer, D.; Schindler, M. *Chem. Phys. Lett.* **1987**, *133*, 293−297.
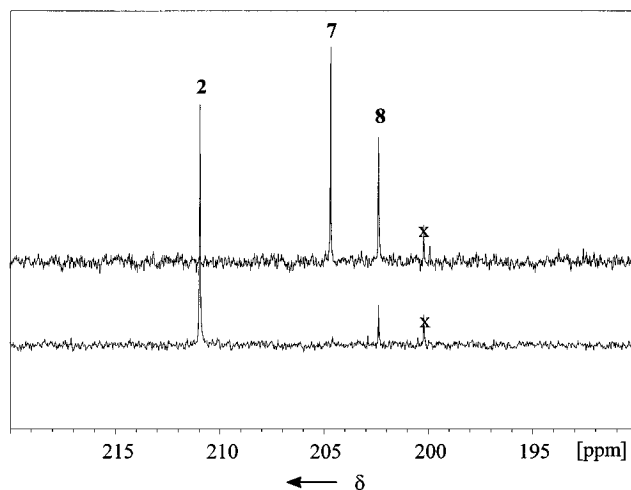
(11) Preliminary ab initio calculations by Cremer et al. suggest hydrogen abstraction with subsequent formation of hydroxyl radicals as the primary step in the rearrangement. D. Cremer, personal communication.
(12) **2** was isolated and characterized in an argon matrix at 10 K by irradiation ($\lambda = 495$ nm) of **4**: UV−vis (Ar, 10 K) $\lambda_{max} = 394$ nm; IR (Ar, 10 K) ν (relative intensity) = 1611.5 (83), 1568.2 (42), 1450.8 (46), 1430.4 (100), 876.7 (33, ν_{O-O}), 850.3 (50) cm^{-1}. Kirschfeld, A. Ph.D. Dissertation, Braunschweig, Germany, 1995.
(13) Dunkin, I. R.; Bell, G. A. *Tetrahedron* **1985**, *41*, 339−347.
(14) Sander, W. *Angew. Chem.* **1986**, *98*, 255−6; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 255−257.
(15) Sander, W. *J. Org. Chem.* **1989**, *54*, 333−339.
(16) Bucher, G.; Sander, W. *Chem. Ber.* **1992**, *125*, 1851−1859.
(17) Wierlacher, S.; Sander, W.; Marquardt, C.; Kraka, E.; Cremer, D. *Chem. Phys. Lett.* **1994**, *222*, 319−324.
(18) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517−1520.