

Dimesitylketone O-oxide: verification of an unusually stable carbonyl oxide by NMR chemical shift calculations

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Abstract

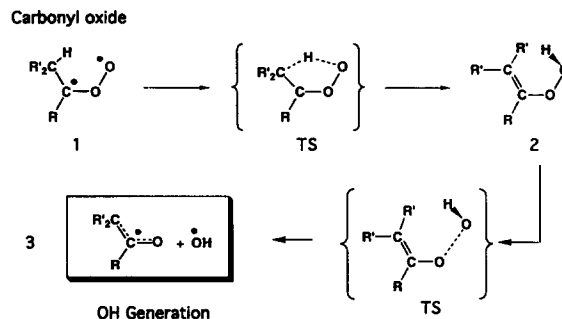
NMR chemical shift calculations in combination with geometry optimizations both based on density functional theory were used to identify and to describe dimesitylketone O-oxide (**6**), which is the first carbonyl oxide that could be generated in solution at -78°C and investigated by NMR spectroscopy. The conformation of carbonyl oxide **6** is characterized by two orthogonal mesityl rings and a close O,H contact between one of the H atoms of the mesityl methyl groups and the terminal O atom of the carbonyl oxide. The calculated geometry and conformation of **6** are verified by the agreement of calculated and measured NMR chemical shifts. The unusual rearrangement of **6** to an alcohol is explained.

1. Introduction

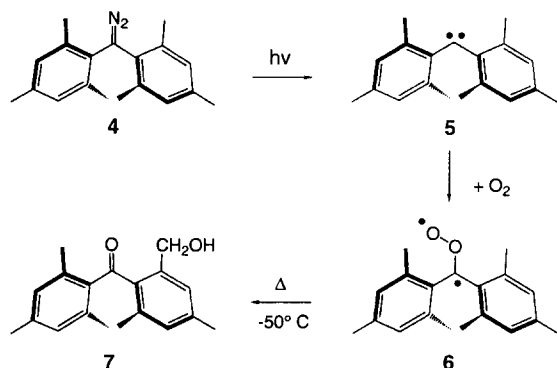
Carbonyl oxides (**1**) play an important role in many oxidation processes, in particular in the ozonolysis of alkenes [1,2]. Recently, Cremer and co-workers were able to show that **1** probably represents the major source of OH radical generation during the gas phase ozonolysis of alkenes according to the mechanism sketched in Scheme 1 [3].

Provided **1** possesses an alkyl group in the syn position to the terminal O atom, rearrangement to the hydroperoxyalkene **2** is kinetically favoured relative to isomerization of **1** to dioxirane, which so far was considered to be the major rearrangement product of **1** [1,2].

We now provide evidence that the rearrangement process described in Scheme 1 also takes place in condensed phases and even occurs in the case of aryl rather than alkyl substitution of **1**. Our investigation was triggered by a recent article by Sander and co-workers [4] who managed to record an NMR



spectrum of a carbonyl oxide in solution. These authors photochemically decomposed the diazo compound **4** (Scheme 2) to generate the carbene **5** in an oxygen-doped $\text{CFCl}_3\text{-BrF}_2\text{CCF}_2\text{Br}$ glass at 77 K. After melting of the glass and warming up to -78°C dimesitylketone O-oxide **6** was identified by the measured ^1H and ^{13}C NMR spectra. It was found that the ^{13}C shift of the COO unit (211 ppm) signifi-



cantly differs from theoretical predictions [5] made in the 1980s for the parent compound H_2COO (**1a**). Upon warming **6** to -50°C , the alcohol **7** was formed as an unusual rearrangement product of a carbonyl oxide. Alternatively, **6** could be photochemically rearranged to dimesityldioxirane (**8**) or decomposed to dimesitylketone (**9**), which did not leave any doubt that **6** is the expected diarylketone O-oxide [4].

In this work, we provide a detailed account of the geometry and conformation of **6**. In addition, we report reliable NMR chemical shift values for **1** that will help to identify **1** in the presence of aldehydes, ketones or dioxiranes. In the case of **6**, calculated and measured NMR chemical shifts are used to verify its geometry and to characterize its electronic structure. Utilizing the calculated properties of **6**, we will show that the mechanism for the reaction $\text{6} \rightarrow \text{7}$ is similar to that described in Scheme 1.

2. Computational methods

Since the investigation of **1** requires highly correlated ab initio methods such as coupled cluster (CC)

theory [6] and since the latter are not feasible for geometry optimizations of molecules with 43 atoms and 123 geometrical parameters, we refrained from using these methods and instead used density functional theory (DFT). We tested various functionals with regard to their ability to describe **1a** using CCSD(T) (CC calculations with all single (S) and double (D) excitations and a perturbative treatment of all triple (T) excitations [6]) geometry of **1a** as appropriate reference [7]. Comparisons suggested that the most reliable account of the geometry and energy of **1** is provided by Becke's three-parameter functional B3LYP [8,9] using the 6-31G(d,p) or, alternatively, 6-31G(d) basis set [10]. Accordingly, B3LYP/6-31G(d) calculations were used to determine the geometry and conformation of **6**.

Sum-over-states density functional perturbation theory (SOS-DFPT) [11] and Hartree-Fock (HF) theory both based on the "individual gauge for localized orbitals" (IGLO) scheme of Kutzelnigg and Schindler [12] were employed to calculate ^1H , ^{13}C , ^{17}O NMR chemical shifts for **6**. At the DFT level, a combination of the Becke exchange [13] and the PW91 correlation functionals [14] rather than B3LYP was used since the former is known to lead to somewhat better shift values [15]. As appropriate basis sets the (9s5p1d/5s1p) [5s4p1d/3s1p] and (11s7p2d/6s2p) [7s6p2d/4s2p] sets were employed, which are of VTZ + P and VQZ + 2P quality and which have been designed by Kutzelnigg and co-workers [16] for NMR chemical shift calculations with the IGLO method. All DFT calculations were based on an accurate calculation of the Coulomb part and numerical integration of the exchange-correlation potential [15]. The well-known deficiencies of DFT methods to lead to occupied orbitals with relatively high energies and, accordingly, to an overestimation of paramagnetic contributions to chemical shifts [17] was compensated by adding appropriate

Table 1
Calculated geometries of some carbonyl oxides R_2COO with $\text{R} = \text{H}$, methyl or mesityl^a

Molecule	Method/basis	OO (Å)	CO (Å)	COO (°)	CR _{syn} (Å)	CR _{anti} (Å)	OCR _{syn} (°)	OCR _{anti} (°)
H_2COO (1a)	CCSD(T)/TZ + 2P	1.355	1.276	117.0	1.080	1.078	118.7	115.0
	B3LYP/6-31G(d,p)	1.343	1.266	119.3	1.086	1.084	199.1	115.5
$(\text{CH}_3)_2\text{COO}$ (1b)	B3LYP/6-31G(d,p)	1.370	1.276	117.3	1.478	1.490	118.7	116.0
(mesityl) ₂ COO (6)	B3LYP/6-31G(d)	1.364	1.294	121.2	1.475	1.477	121.4	112.9

^a The following abbreviations are used: R = H or C; TZ + 2P: (11s6p3d/5s3p)[5s3p2d/3s2p], Ref. [6].

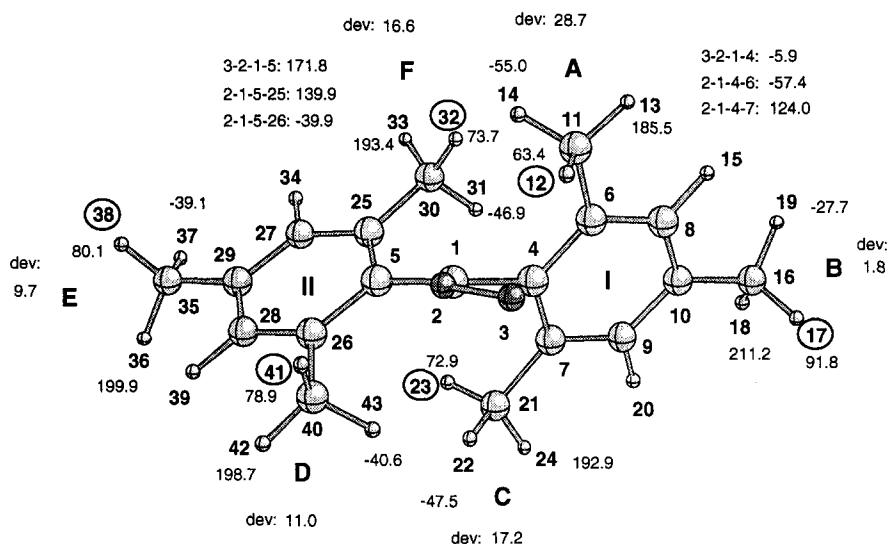


Fig. 1. B3LYP/6-31G(d) conformation of dimesitylketone O-oxide **6**. Numbering of atoms and labelling of methyl groups is indicated. Calculated dihedral angles (in $^{\circ}$) are given, if not specified, for the atom sequence C(lowest label)–C(ring)–C–H. Methyl H atoms with dihedral angles close to 90° are encircled. The value ‘dev’ denotes the average deviation of dihedral angles of a methyl group from the ideal values of the toluene methyl group. Atoms 2 and 3 are the O atoms of the COO unit.

level shift factors to orbital energy differences as was first suggested by Malkin and co-workers [18] and studied in detail by Olsson and Cremer [15]. Chemical shift calculations were carried out with the program package COLOGNE96 [19] while for the geometry optimizations the Gaussian 94 ab initio program package was used [20].

3. Results and discussion

Reliable CCSD(T)/TZ + 2P calculations show that the 4π system of **1a** is characterized by a relatively long CO bond of 1.28 Å and a relatively short OO bond of 1.36 Å (see Table 1). Previous investigations have shown that correlation corrected ab initio calculations at lower levels of theory fail to predict the correct ratio of the CO and OO distances by either equalizing bond lengths too much (MP2, MP4) or exaggerating their difference too strongly (HF, MP3) [6]. As revealed by the data in Table 1, B3LYP/6-31G(d,p) calculations reproduce the CCSD(T) geometry surprisingly well (CO: 1.27 Å; OO: 1.34 Å) thus indicating that the amount of electron correlation covered by DFT methods suffices for the description of carbonyl oxides. Accord-

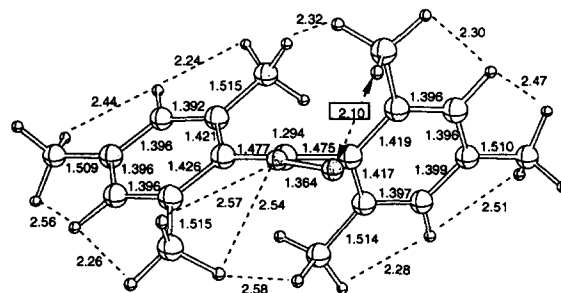


Fig. 2. B3LYP/6-31G(d) geometry of dimesitylketone O-oxide **6**. All distances in Å. Non-bonded distances are indicated by dashed lines. The contact distance between H12 and O3 is framed for better visibility.

ingly, the B3LYP/6-31G(d) geometry of **6** shown in Fig. 1 (numbering and conformational data) and Fig. 2 (distances) can be considered as being rather reliable.

Arrangement of the mesityl rings either in or perpendicular to the COO plane leads to strong steric repulsion between the four *o*-positioned methyl groups of **6**. Therefore, the two mesityl groups are rotated by 40 and 57° in opposite directions out of the COO plane so that the phenyl rings are almost perpendicular to each other. The two mesityl groups

are only slightly deformed in the equilibrium conformation as is reflected by the fact that their heavy atom framework is planar with a maximal out-of-plane deviation of 2°. The average CC ring bond lengths in rings I and II (Fig. 1) are 1.404 and 1.405 Å with standard deviations of just 0.010 and 0.013 Å, respectively (Fig. 2). The CCH₃ bonds vary between 1.506 and 1.515 Å, which is close to the corresponding toluene value. Angle distortions from ideal sp² hybrid angles of 120° are such (all < 4°) that steric repulsion between the methyl H atoms and adjacent C_{ring}H groups are lowered.

In toluene, the methyl group adopts a form in which one CH bond is in the plane perpendicular to

the ring plane while the other two CH bonds form dihedral angles of 30 and -30° with adjacent ring bonds. In **6**, methyl groups B, C, D, E, and F (Fig. 1) are slightly rotated out of these positions by 2 (B), 17 (C), 11 (D), 10 (E), and 17° (F) on average. In this way, the non-bonded H,H contact distances (indicated by dashed lines in Fig. 2) are 2.24–2.60 Å (or longer), which is in the range of typical H,H van der Waals distances.

The only exception is methyl group A, which is rotated by 29° out of the toluene conformation thus leading to enhanced electrostatic attraction between H12 and the terminal O atom of the COO group. The distance between these atoms is 2.10 Å and, by this,

Table 2
Calculated NMR chemical shifts of carbonyl oxides, their isomeric dioxiranes and appropriate reference compounds^a

		HF-IGLO		SOS-DFPT		Exp. ^c
		VTZ + P		VTZ + P	VQZ + 2P	
		MP2 ^b	B3LYP	B3LYP	B3LYP	
¹³ C chemical shifts						
H ₂ C=O			198.1	187.8	194.6	197.0
H ₂ COO (1a)		227.0	221.7	179.9	198.2	
c-H ₂ COO		82.6	87.9	89.2	91.4	
(CH ₃) ₂ C=O		CO	209.7	212.6	199.6	208.2
		CH ₃	23.7	31.6	23.0	30.7
(CH ₃) ₂ COO (1b)		CO		249.9	207.5	216.6
		CH ₃ , syn		26.6	23.4	24.5
		CH ₃ , anti		28.6	24.1	25.4
c-(CH ₃) ₂ COO (8)		CO	99.2	100.5	104.0	102.3
		CH ₃	17.0	25.6	23.0	22.7
(mesityl) ₂ C=O (9)		CO				202.5
(mesityl) ₂ COO (6)		CO		243.4	210.6	211.0
¹⁷ O chemical shifts						
HO-OH			190	200	214	210
H ₂ C=O			776	671	700	(685)
H ₂ COO (1a)		O _c	770	717	647	(665)
		O _i	820	822	977	(987)
c-H ₂ COO			250	239	271	277
(CH ₃) ₂ C=O			680	673	608	638
(CH ₃) ₂ COO (1b)		O _c		561	558	586
		O _i		766	893	904
c-(CH ₃) ₂ COO (8)			330	284	316	334
(mesityl) ₂ COO (9)		O _c		553	582	(596)
		O		719	939	(948)

^a NMR chemical shifts in ppm relative to TMS (¹³C) and gaseous H₂O (¹⁷O). c-H₂COO and c-(CH₃)₂COO denote dioxirane and dimethyldioxirane.

^b HF-IGLO values at MP2/6-31G(d) geometries from Ref. [5].

^c Experimental values from Ref. [25] (H₂CO, (CH₃)₂CO), Ref. [23] (dimethyldioxirane), Ref. [4] (dimesitylketone O-oxide, ketone **9**), Ref. [22] (HOOH, acetone). Values in parentheses are estimated as described in the text.

0.3 Å shorter than the van der Waals distance of 2.4 Å between an H and an O atom [21]. We found similar H12–O distances in preliminary calculations of **6** carried out at the HF/3-21G and B3LYP/3-21G level and, therefore, conclude that the close contact between H12 and terminal O is not an artefact of the method used, but describes a stabilizing attraction between these atoms.

The geometry of the COO group of **6** (CO: 1.36 Å, OO: 1.29 Å) resembles that of dimethylcarbonyl oxide **1b** (CO: 1.37 Å; OO: 1.28 Å; see Table 1). There are slight differences of 2–3° in the OOC and OCC angles as one could expect from the increase in steric interactions between two mesityl groups as compared to two methyl groups. The calculated C1C bonds (1.48–1.49 Å, Table 1) do not indicate any residual conjugative stabilization between COO group and phenyl rings rotated by 57 and 40°. All calculated geometrical parameters suggest that in the equilibrium conformation strong steric repulsion is avoided.

In Table 2, SOS-DFPT ¹³C and ¹⁷O NMR chemical shifts of carbonyl oxides, dioxiranes, and some appropriate reference compounds are compared with the corresponding HF-IGLO and available experimental values. In previous work, we have shown that SOS-DFPT leads to reliable NMR chemical shifts also in those cases in which correlation corrections play an important role [5]. According to the data in Table 2, both HF-IGLO and SOS-DFPT-IGLO ¹³C chemical shifts of aldehydes and dioxiranes are in reasonable agreement with experiment. However, there is a large difference of 20–40 ppm between the HF-IGLO and the SOS-DFPT ¹³C shift of **1a** (Table 2) indicating that the former method fails in this case. Previous HF-IGLO estimates of NMR chemical shifts of carbonyl oxides (also included in Table 2) [5] are flawed due to limitations of the methods available in the 1980s for calculating molecular geometries and NMR chemical shifts of **1**.

Considering SOS-DFPT results as the more reliable ones, the following observations can be made with regard to NMR chemical shifts of ketones, carbonyl oxides, and dioxiranes.

(1) The ¹³C chemical shifts of the CO carbon are similar for ketones and carbonyl oxides both being in the region 200–210 ppm. For **1b**, the CO carbon is shifted downfield by 7–8 ppm relative to the CO

carbon of acetone. This is in line with a downfield shift of 8.6 ppm observed experimentally for **6** and ketone **9** [4].

(2) The ¹³C chemical shift of a dioxirane occurs at about 100–110 ppm and, therefore, can be clearly distinguished from that of the corresponding carbonyl oxide.

¹⁷O NMR chemical shifts of ketones are known to strongly depend on the solvent used [22]. Shift differences of 65 ppm have been reported for acetone depending on whether measurements have been made in neat liquid, aqueous solution or alkane solutions [22]. The corresponding gas phase value of acetone should be close to 624 ppm, which is neither reproduced by HF-IGLO nor DFT-IGLO calculations [15]. We find that SOS-DFPT with the VTZ + P basis set underestimates the chemical shift value while calculations with the VQZ + P basis overestimate it by about the same amount so that an average of calculated values represents a reasonable estimate of the experimental gas phase value. These estimates have been included in Table 2 and they are the basis for the following conclusions.

(3) The ¹⁷O chemical shift of the central O (O_c) of a carbonyl oxide appears about 50 ppm upfield of that of the keto oxygen of the corresponding ketone. The ¹⁷O shift of the terminal O is about 275 ppm downfield shifted from the CO oxygen of the ketone. Hence, it should be easy to detect carbonyl oxides in the presence of the corresponding ketones with the help of their ¹⁷O NMR spectrum.

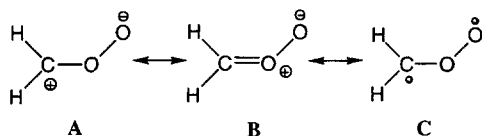
(4) The ¹⁷O chemical shift of dimethyldioxirane has been measured at 338 ppm (relative to gaseous H₂O) [23], which is correctly reproduced by SOS-DFPT calculations in line with the fact that ¹⁷O chemical shifts of peroxide oxygens are calculated reliably at this level of theory (compare with HOOH in Table 2) [15].

DFT results obtained with the VTZ + P basis suggest a ¹³C chemical shift of 210.6 for **6** that is within 0.4 ppm of the measured ¹³C chemical shift [4]. The ¹⁷O NMR chemical shifts should be at 600 and 950 ppm, clearly separated from the (estimated) ¹⁷O shift of ketone **9** at 650 ppm [4].

It is interesting to discuss the NMR chemical shifts of a carbonyl oxide in connection with its electronic structure.

Synthetic chemists prefer to view **1** as a 1,3-di-

polar compound or zwitterion described by the resonance forms **A** and **B**



while theoreticians tend to describe **1** as biradical **C** which attains zwitterionic character only by substitution and/or environmental effects. Both descriptions are speculative since **1** will be best described by a superposition of all three resonance forms **A**, **B**, and **C**. CCSD(T) and B3LYP geometries as well as calculated ^{13}C and ^{17}O chemical shifts of **1** suggest that the molecule is not a pure biradical, but possesses up to 20% zwitterionic character.

In Fig. 3, calculated NMR chemical shifts are compared with the available experimental shifts [4]. With the help of calculated ^1H shifts, all NMR shifts measured by Sander and co-workers [4] can be assigned to the various methyl and phenyl protons of **6**. Methyl rotation at the temperature of measurement leads to averaged ^1H values, which disguise some interesting effects.

Proton H12 is considerably deshielded and possesses a shift value (3.74 ppm) typical of vinyl rather than methyl protons. The calculated shift value is indirectly confirmed by measured proton shifts that give for one methyl group a ^1H shift of 2.53 ppm, which is 0.3–0.9 ppm higher than the averaged shifts of the other methyl groups [4]. Hence, one of the ^1H shifts of this particular methyl group should be 1–2 ppm downfield shifted compared to those of the other H atoms. Our calculations indicate that methyl group A and H12 are responsible for the shift at 2.53 ppm (calculated 2.48 ppm, Fig. 3) and that this value confirms the close contact between H12 and the terminal O atom of the COO unit.

Cremer and co-workers have recently shown that in the gas phase such a close contact is the prerequisite for an H shift from a neighbouring methyl group to the terminal O atom of **1** leading to the hydroperoxide **2** and its subsequent dissociation into OH and alkyl radicals **3** (Scheme 1) where the fate of the radicals depends on the reaction system [3]. These authors have also predicted that for syn-alkyl **1** this reaction sequence is more likely than the generally assumed rearrangement to isomeric dioxirane [3]. In the solution phase, **1** will be formed in a solvent cage either in the form of a dipole complex with an aldehyde if **1** is generated in the course of the ozonolysis [24] or by itself if generated in an

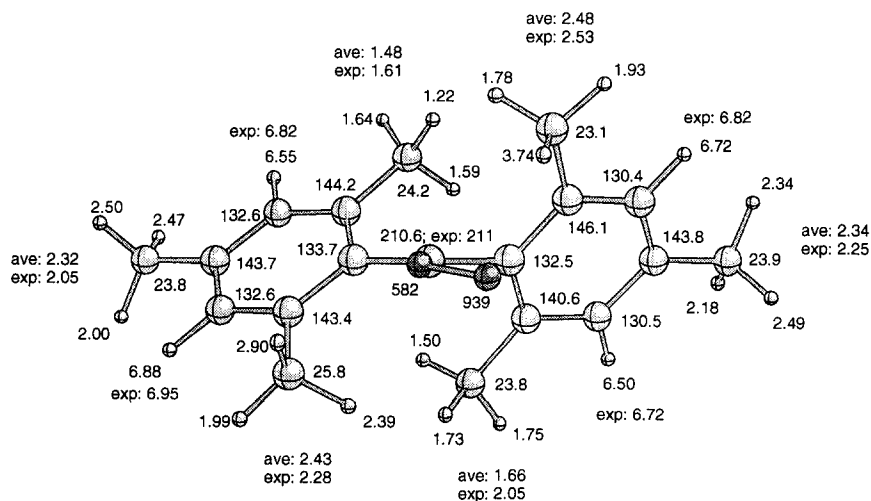
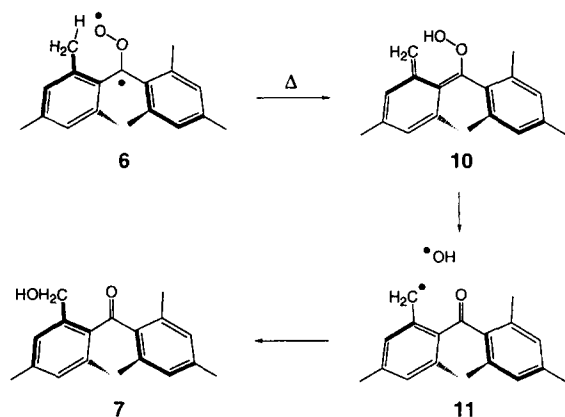


Fig. 3. SOS-DFPT NMR chemical shifts in ppm relative to TMS (^1H and ^{13}C) and gaseous H_2O (^{17}O) for dimesitylketone O-oxide **6**. For methyl groups averaged values 'ave' are compared with the corresponding experimental ('exp') values measured by Sander and co-workers [4].



Scheme 3.

O_2 -doped matrix at low temperature. The solvent cage makes it likely that the OH radical and alkyl radical are kept together for some time and that a recombination of these radicals to yield the alcohol 7 is most likely. The most likely reaction mechanism leading from 6 via hydroperoxide 10 and radical 11 to alcohol 7 is shown in Scheme 3.

In conclusion, our calculations have led to the following results.

(1) According to NMR chemical shift calculations, the carbene oxidation product 6 investigated by NMR spectroscopy at -78°C is indeed the first carbonyl oxide investigated in solution.

(2) The geometry and conformation of 6 are characterized by a close contact between a methyl H and the terminal O atom of the COO unit.

(3) Calculations provide evidence for a new rearrangement mechanism of carbonyl oxides in the solution phase that has recently been postulated for the gas phase [3].

In view of this new reaction possibility of 1 in solution it is advisable to reconsider previous mechanistic studies of reactions in solution that involve 1 [2].

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