Sterically Hindered Carbonyl *O*-Oxides and Dioxiranes – (6-*tert*-Butyl-2,3,4-trimethylphenyl)phenylcarbonyl *O*-Oxide and (6-*tert*-Butyl-2,3,4-trimethylphenyl)phenyldioxirane

Kerstin Schroeder,[a] and W. Sander*[a]

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(6-*tert*-Butyl-2,3,4-trimethylphenyl)phenylcarbonyl *O*-oxide (**1b**) was generated by photooxidation of diazo compound **6b** in an organic glass and in solution and characterized by UV/Vis spectroscopy and by its photo- and thermochemistry. With 4.5 min at 230 K the half-life of **1b** is considerably smaller than that of dimesityl ketone *O*-oxide (**1a**). The only clearly detected thermal product of **1b** is the corresponding ketone **3b**. The isomeric (6-*tert*-butyl-2,3,4-trimethylphenyl)-phenyldioxirane (**2b**) could also be synthesized and characterized by NMR spectroscopy. With a half-life time of 20 min at 20 °C this dioxirane rearranges to the isochroman derivative **11** as the only product. Plausible mechanisms for this rearrangement, which involves the hydroxylation of a non-activated C–H bond, are discussed.

Introduction

Carbonyl *O*-oxides **1** and dioxiranes **2** are unusual peroxides involved in many organic oxidation reactions.[1–4] During the last years the role of carbonyl oxides in tropospheric chemistry leading to the formation of OH radicals has been discussed.[5–8] Due to the instability of the carbonyl oxides **1**, matrix isolation spectroscopy[1,9–12] and time-resolved laser flash photolysis (LFP)[13,14] have been used for the spectroscopic characterization of these species. Carbonyl oxides **1** are proposed to be key intermediates in the ozonolysis of olefins (Criegee mechanism)[15,16] while applications as oxygen transfer reagents in synthesis are very limited, so far.[17] Dimesityl ketone *O*-oxide (**1a**) with two bulky mesityl groups blocking the C–O–O group was shown to be stable at −80 °C in a variety of solvents.[18] This allowed the characterization of **1a** by NMR spectroscopy. At higher temperatures **1a** rapidly decays to give a mixture of ketone **3a** and the C–H insertion product of an oxygen atom **4**.

In contrast, several of the isomeric, more stable dioxiranes **2** have found applications as mild oxygen transfer reagents.[19,20] In most instances, a solution of dimethyldioxirane in acetone, which can be conveniently synthesized, is used as reagent.[21,22] Other dioxiranes are generated in situ without isolation and are directly used as oxygen transfer reagents.[23,24]

Important applications of dioxiranes are epoxidations,[25,26] oxygen transfer to heteroatoms (mainly P and S), and hydroxylations of non-activated C–H bonds. The mechanism for the latter, highly interesting reaction is controversial. Both concerted[24,27,28] and non-concerted (via diradicals)[29] mechanisms have been discussed for the oxidation of alkanes with dioxiranes.[30] Yang et al. proposed a concerted oxygen insertion mechanism for the intramolecular oxidation of unactivated C–H bonds by dioxiranes generated in situ.[23,24] In this mechanism an oxygen atom is inserted into a C–H bond via a spiro transition state leading to a hydroxy ketone. The hydroxy ketone eventually forms a hemiketal. The observed regioselectivity – δ-selectivity vs. γ-selectivity as expected for radicals – was taken as evidence for the concerted mechanism.

In a recent computational study by Sarzi-Amadè et al., on the other hand, it was found that the hydroxylation of C–H bonds with dioxiranes preferentially proceeds by hydrogen abstraction and radicaloid transition states.[29] Moreover, these authors proposed a collinear and a perpendicular approach of the H atom to the O–O bond, with the latter being more favorable. An inspection of the transition states for the oxygen insertion proposed by Yang et al. reveals a similarity between their favored "spiro" transition state and the perpendicular diradicaloid transition state of the hydrogen abstraction. Accordingly, their disfavored "planar" transition state is similar to the collinear diradicaloid transition state of the hydrogen abstraction.

The only dioxirane that has been isolated in substance and characterized by X-ray crystallography is dimesityldioxirane (**2a**).[2,31,32] This dioxirane is synthesized by photooxidation of dimesityldiazomethane and forms colorless

[a] Lehrstuhl für Organische Chemie II der Ruhr-Universität, 44780 Bochum, Germany

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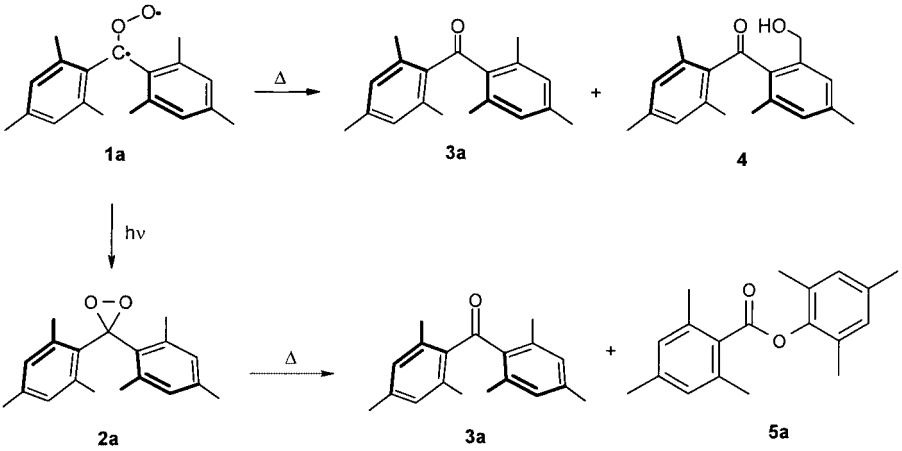
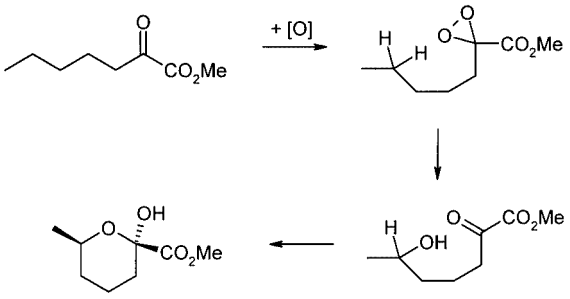




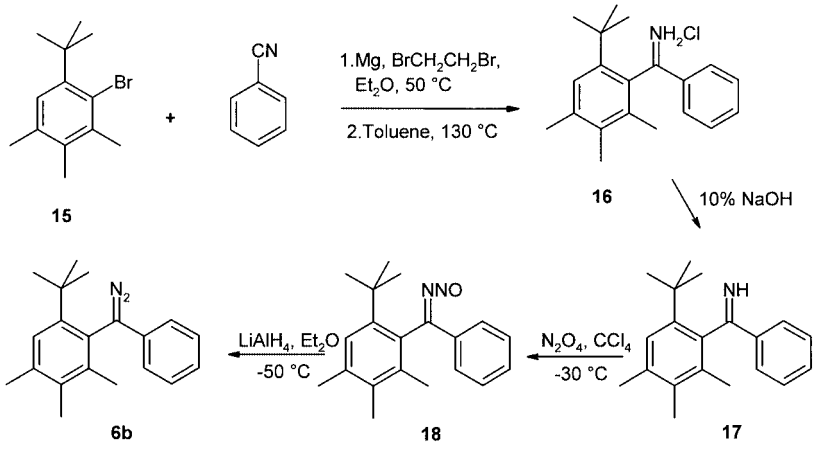
crystals with a half life of 55 h at 20 °C. The thermal decomposition yields dimesityl ketone (**3a**) (loss of one oxygen atom) and ester **5a** (rearrangement).

Here we describe the synthesis and spectroscopic characterization of (6-*tert*-butyl-2,3,4-trimethylphenyl)phenylcarbonyl *O*-oxide (**1b**) and (6-*tert*-butyl-2,3,4-trimethylphenyl)phenyldioxirane (**2b**). One side of these molecules is sterically crowded with the highly substituted phenyl ring, while the other side is substituted by phenyl only and thus more easily accessible. A comparison of the thermal stability of **1b** and **2b** with that of the dimesityl systems **1a** and **2a** should provide insight into the conditions required for the synthesis of thermally stable carbonyl oxides and dioxiranes.

Results and Discussion

(6-*tert*-Butyl-2,3,4-trimethylphenyl)phenylcarbonyl *O*-Oxide (1b)

Precursor of both **1b** and **2b** is (6-*tert*-butyl-2,3,4-trimethylphenyl)phenyldiazomethane (**6b**) which is synthesized by nitrosation of the corresponding ketimine **17** to **18** followed by reduction with $LiAlH_4$ (Scheme 1). The diazomethane **6b** forms red-violet crystals which dissolve in CCl_3F as a red solution with an absorption maximum at 494 nm. Irradiation ($\lambda > 515$ nm) of **6b** in an oxygen-saturated organic glass [1:1 mixture of CCl_3F and $(CBrF_2)_2$] at 78 K results in the appearance of a new broad band with a maximum at 380 nm (Figure 1), simultaneously the glass turns intense yellow. Subsequent irradiation with blue light ($\lambda >$ 420) rapidly leads to the bleaching of this new absorption. In the absence of oxygen the yellow compound is not formed. This observation is completely analogous to the formation of carbonyl oxide **1a** from dimesityldiazome-



Scheme 1. Synthesis of diazo compound **6b**

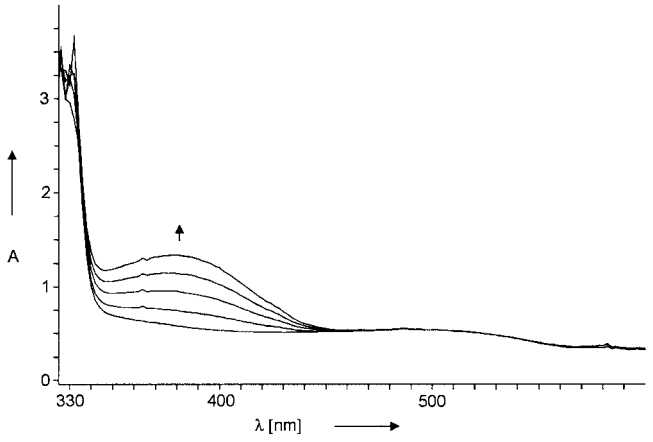


Figure 1. UV/Vis spectra showing the formation of carbonyl oxide **1b** in an organic glass; irradiation ($\lambda > 515$ nm) of diazomethane **5b** dissolved in oxygen-saturated $CCl_3F/(CBrF_2)_2$ (1:1) at 78 K; the absorption with a maximum at 380 nm is growing in

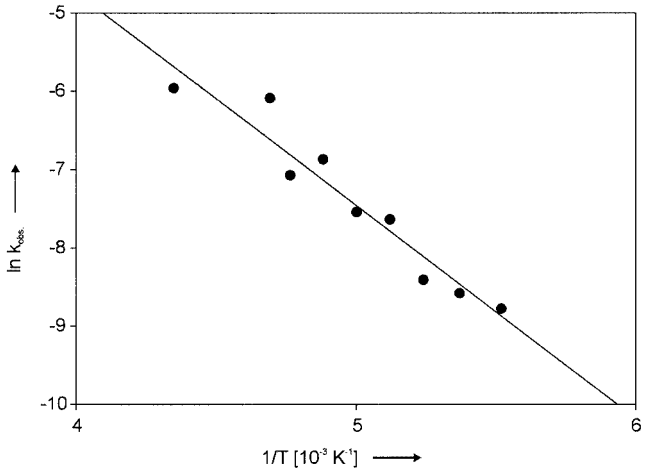
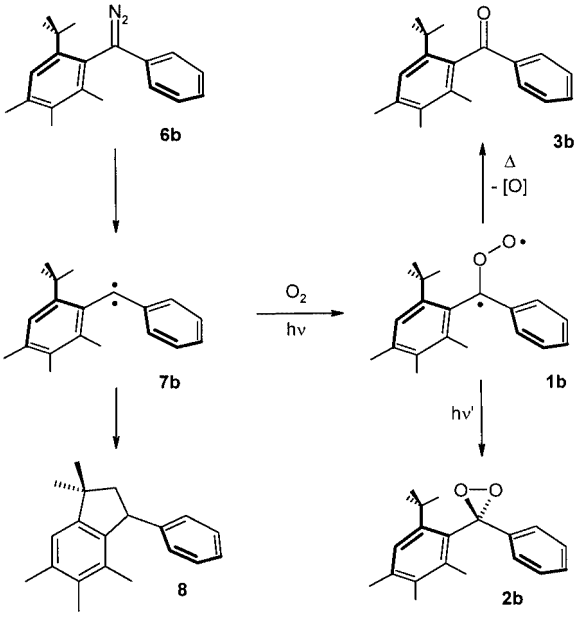


Figure 2. Arrhenius plot of the thermal decay of carbonyl oxide **1b** in $CCl_3F/(CBrF_2)_2$ (1:1) in the temperature range between 181 and 230 K; the decrease of the strong absorption with $\lambda_{max} = 380$ nm is monitored

thane (**6a**), and thus the yellow compound is assigned to carbonyl oxide **1b** (Scheme 2). Thus, irradiation of **6b** produces the short-lived carbene **7b** which is rapidly trapped by molecular oxygen to give **1b**. A by-product isolated after warming the mixture to room temperature is the indane derivative **8** formed by insertion of the carbene center into a C−H bond of the *tert*-butyl group (Scheme 2) and ketone **3b**.

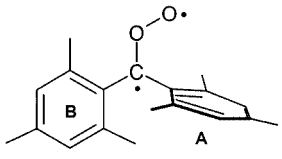


Scheme 2. Synthesis of carbonyl oxide **1b** and dioxirane **2b** by photooxidation of diazo compound **6b**

The carbonyl oxide **1b** could also be synthesized in oxygen-saturated $CCl_3F/(CBrF_2)_2$ (1:1) solution at temperatures between 181 and 230 K, which allowed to study its thermal decay. At all temperatures a first-order decay kinetics was observed with a half life time between 75 min (181 K) and 4.5 min (230 K). From the Arrhenius plot (Figure 2) an activation barrier of 5.4 kcal mol^{-1} is calculated for the thermal decay of **1b**, which is considerably smaller than the 14.7 kcal mol^{-1} of **1a**.

The only thermal product of **1b** identified is ketone **3b**. The fate of the terminal oxygen atom of **1b** is not clear, but most likely the solvent is oxidized. This is in contrast to **1a**, which forms both ketone **3a** and alcohol **4** by formal insertion of the terminal O atom into a C−H bond of an adjacent methyl group. The different reactivity of carbonyl oxides **1a** and **1b** can be rationalized by comparison of their structures calculated at the B3LYP/6-31G(d) level of theory (Figure 3).

The structure of the carbonyl oxide **1a** was determined by NMR spectroscopy and by quantum chemical calculations.[18,33,34] According to DFT calculations **1a** is chiral with the two mesityl rings twisted. The terminal oxygen atom is in close contact with one of the *ortho*-methyl groups which explains the formation of the insertion product **4** as one of the major thermal products. The NMR shows a C_s-symmetrical time-averaged structure with the COO moiety and mesityl ring B lying in the mirror plane. The terminal oxygen atom points towards the perpendicular mesityl ring A. Due to the steric interaction of the *ortho*-methyl groups in the rings A and B, the rotation of the mesityl rings is inhibited and the averaging of the structure occurs by a libration motion.



For carbonyl oxide **1b** two principal conformers have to be considered: *syn*-A with the terminal oxygen atom pointing towards the sterically crowded ring A and *syn*-B with the oxygen atom pointing towards the phenyl ring. In both conformers the phenyl ring B lies nearly in the COO

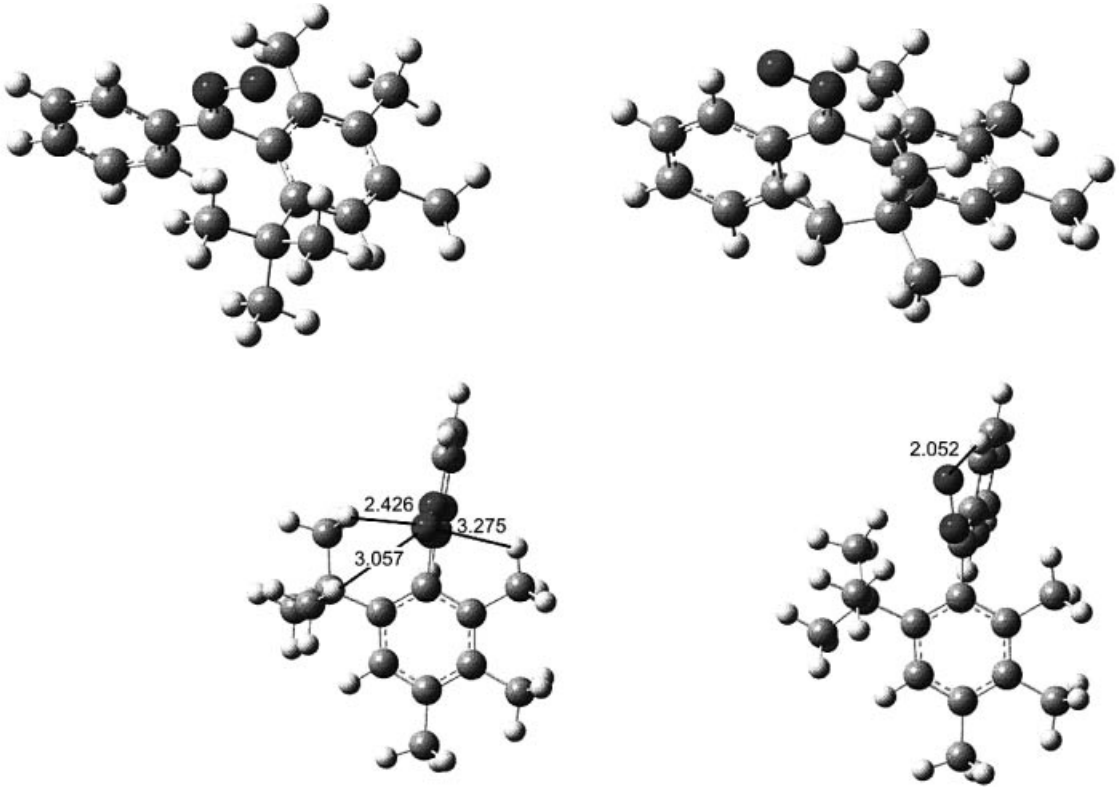
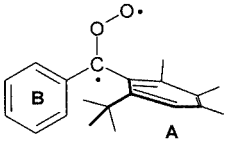


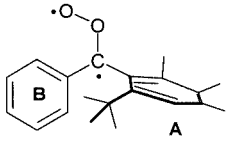
Figure 3. Structure of carbonyl oxides **1b** calculated at the B3LYP/6-31G(d) level of theory; right hand side: conformer *syn*-A; left hand side: conformer *syn*-B

plane while ring B bearing the *tert*-butyl group is perpendicular. Similar to **1a**, the structure *syn*-B of **1b** also exhibits a remarkably short non-covalent interaction between the terminal oxygen atom and a hydrogen atom of ring B (Figure 3). However, since abstraction of this hydrogen atom would lead to a phenyl radical and not to a stabilized benzyl radical as with **1a**, the formation of a phenol as insertion product of the thermal reaction of **1b** is not observed.

Since *syn*-A and *syn*-B are calculated to be energetically nearly degenerate [*syn*-A is calculated to be only 0.16 kcal/mol more stable than *syn*-B at the B3LYP/6-31G(d) level of theory] both conformers are expected to be formed in solution. There is a considerable barrier for the *syn*/*anti* isomerization in carbonyl oxides which prevents equilibration even at higher temperatures,[35−39] and thus both conformers should be able to coexist in solution.



syn-A

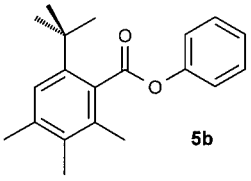


syn-B

(6-*tert*-Butyl-2,3,4-trimethylphenyl)phenyldioxirane (2b)

The dioxirane **2b** was synthesized by photooxidation of diazomethane **6b** in a specially designed photo reactor (Figure 4). The irradiation was carried out in oxygen-saturated CCl_3F at −70 °C using a $CuCl_2$/HCl filtering solution and a mercury arc lamp ($\lambda > 400$ nm). The dioxirane **2b** was purified by HPLC; however, it could not be completely separated from a contaminant which was identified as 4,4,6,7,8-pentamethyl-1-phenylisochroman-1-ol (**11**) (Scheme 3). Dioxirane **2b** is photochemically and thermally unstable which simplifies the assignment of ^{1}H and ^{13}C NMR signals in a mixture with **11**. The characterization of **2b** was achieved by H,C correlation NMR spectroscopy at −20 °C (Figure 5).

The thermal decay of **2b** follows first order kinetics and leads to the isochroman derivative **11** as the only product. This is in contrast to the thermal decay of dioxirane **2a** which produces a mixture of ketone **3a** and ester **5a**. The ketone **3b** and traces of ester **5b** are formed as by-products during the photooxidation of diazo compound **6b**, but not as products of the thermal decomposition of dioxirane **2b**.



5b

The thermal stability of dioxirane **2b** is considerably smaller than that of **2a**. Thus, at 10 °C the half-life times of **2a** and **2b** are 92 min and 109 h, and at 20 °C 20 min and 55 h, respectively. These differences in the thermal

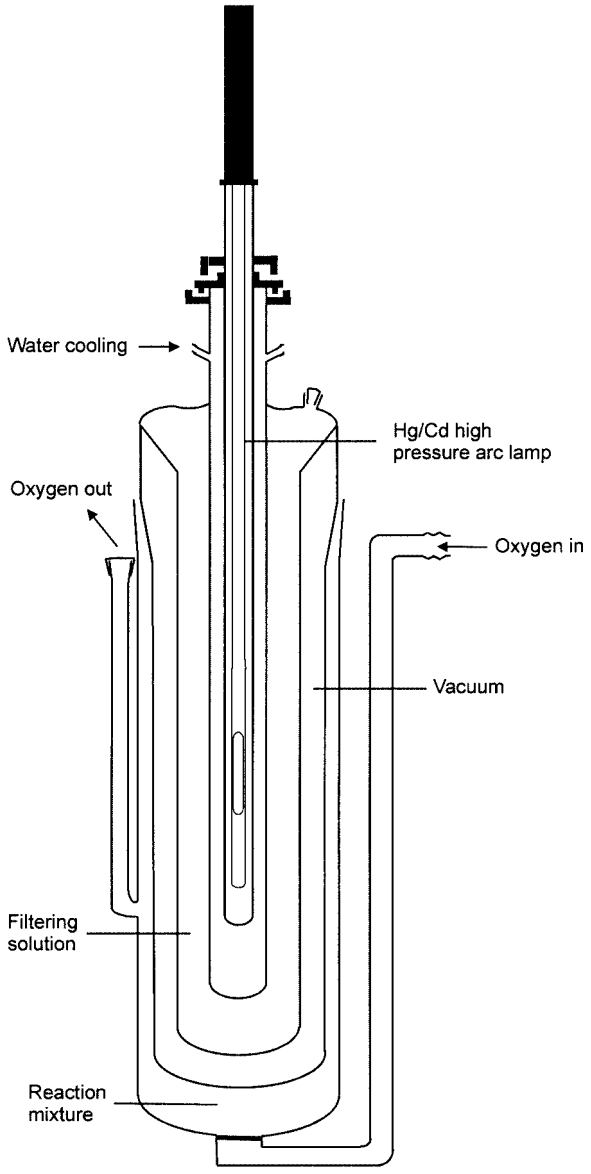


Figure 4. Photoreactor for the synthesis of dioxirane **2b**

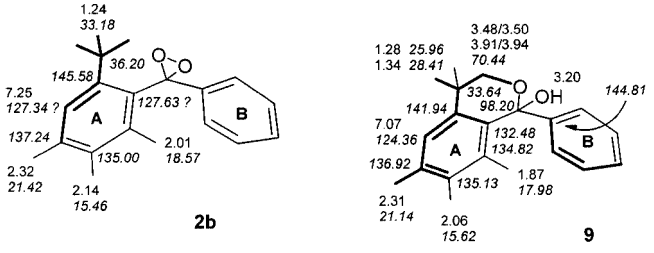


Figure 5. Some NMR spectroscopic data of dioxirane **2b** and its rearranged product **11**; ^{1}H (normal), ^{13}C (italics)

products and in the kinetic stability of **2a** and **2b** indicates a change in the thermal decay mechanism. The first step in the thermolysis of **2a** is most likely the rupture of the O−O bond and formation of dioxy diradical **9**. This diradical is stabilized either by transfer of an oxygen atom to a substrate or solvent molecule to give ketone **3a** or by migration of a phenyl group to give ester **5a**. In both cases the opening of the dioxirane ring is rate-determining.

The rearrangement of **2b** to give **11** requires the cleavage of the O−O bond of the dioxirane ring and of one of the C−H bonds of the *tert*-butyl group and the formation of a new C−O and a O−H bond. The overall process can be described as a self-oxidation of the dioxirane. Three plausible mechanism for the self-oxidation of dioxirane **2b** are outlined in Scheme 3.

Pathway A, Diradical H Abstraction

The first step of Pathway A is the opening of the O−O bond of the dioxirane ring to form dioxydiradical **9**. Diradical **9** abstracts a hydrogen atom from the *tert*-butyl group to produce the second diradical **10** which finally is stabilized by ring-closure to give **11**. Migration of a phenyl group in diradical **10** would lead to diradical **12** which then could produce phenoxyindanol **13**. The phenyl migration would be analogous to the rearrangement in dioxirane **2a** leading to the ester **5a**. However, since **13** is not observed, there is no evidence for the phenyl migration in diradical **10**. The rate-determining step of the reaction sequence of Pathway A should be the opening of the O−O bond.

Pathway B, Concerted H Abstraction

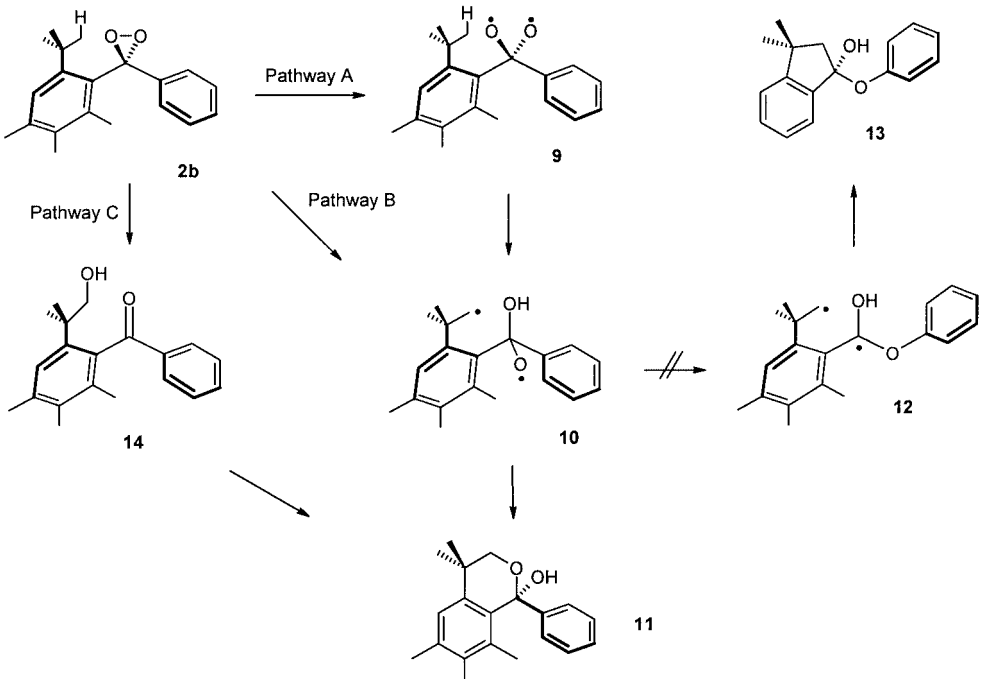
The only difference to pathway A is that the hydrogen abstraction is concerted and diradical **10** is directly formed from **2b** via a diradicaloid transition state. This reaction step should be rate-determining.

Pathway C, Concerted O Insertion

The first step in this reaction sequence is the insertion of one of the dioxirane O atoms into a C−H bond of the *tert*-butyl group. The primary product is now hydroxy ketone **14** while diradicals are not formed as intermediates. Hydroxy ketone **14** could subsequently form **11** as its hemiketal. Since the latter step should also have an appreciable activation barrier (compared to radical recombinations) both steps could be rate-determining. If the activation barrier of the second step is higher than that of the first step, **14** should built up as an intermediate during the reaction.

The kinetics of the decay of **2b** was monitored by ^{1}H NMR spectroscopy in $CDCl_3$ at 10 °C. Under these conditions it follows clean first-order kinetics, and **11** is the only product that can be detected. Other intermediates such as **14** are not observed. Although we cannot rigorously exclude Pathway C, the absence of **14** as an intermediate makes this reaction sequence unlikely.

The geometric parameters of dioxirane **2b** calculated at the B3LYP/6-31G(d) level of theory are very similar to that of **2a**. For the latter the comparison of the calculated one with the X-ray crystallographic structure reveals a good agreement of the calculated and experimental bond angles of the dioxirane ring and the C−O bond lengths



Scheme 3. Mechanisms for the thermal decay of dioxirane **2b**

(Table 1).[32] Only the calculated O−O distance of 1.491 Å is slightly shorter than the experimental value of 1.503 Å. With 1.494 Å the calculated O−O distance in **2b** is slightly larger than that in **2a** which indicates a smaller steric pressure (buttressing effect) on the dioxirane ring.

Table 1. Some geometric data of dimesityldioxirane (**2a**) and (6-*tert*-butyl-2,3,4-trimethylphenyl)phenyldioxirane (**2b**)

	r(O−O) [Å]	*r*(C−O) [Å]	θ(OCO) [°]	θ(RCR) [°]
2a:				
X-ray structure[a]	1.503(5)	1.414(4)[b]	64.2(3)	119.2(4)
B3LYP/6-31G(d)	1.490	1.414	63.6	120.5
2b:				
B3LYP/6-31G(d)	1.494	1.414[c]	63.8	119.2

[a] Ref.[32] [b] Average between 1.413(5) Å and 1.414(5) Å. [c] Average between 1.418 and 1.410.

Interesting is the short non-bonding O···H contact of 2.206 Å between one of the oxygen atoms and a hydrogen atom of the *tert*-butyl group (Figure 6) which explains the lower thermal stability of **2b** compared to **2a**. This hydrogen atom is target of the hydrogen abstraction (or less likely oxygen insertion) leading to the formation of **11**. For **2a** the shortest O···H contact is 2.467 Å calculated and 2.346 Å according to the X-ray structure and thus loss of oxygen or migration of a mesityl group is the preferred reaction.

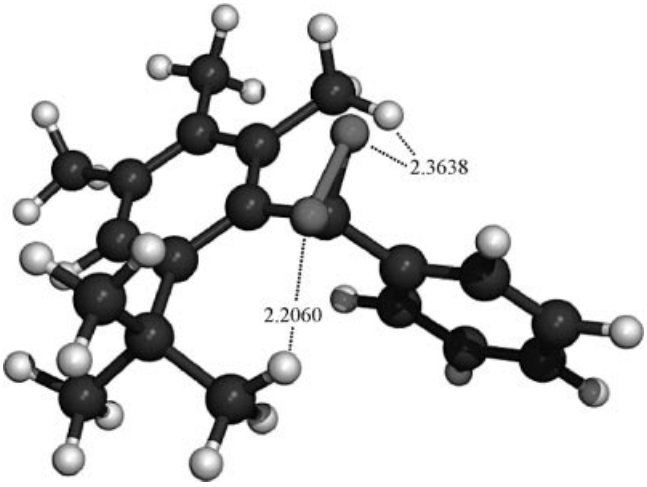


Figure 6. Structure of dioxirane **2b** calculated at the B3LYP/6-31G(d,p) level of theory

Conclusion

Carbonyl oxide **1b** and dioxirane **2b** are interesting new oxygen transfer reagents that could be characterized in solution. Both molecules are considerably less stable than the dimesityl-substituted systems **1a** and **2a**. Part of this reduced stability might be caused by the less efficient steric shilding of a phenyl group compared to a mesityl group. For **2b** the lifetime is reduced by the internal oxidation of the *tert*-butyl group. Both oxygen insertion or hydrogen ab-

straction have to be considered as the primary reaction step, although the latter seems to be more consistent with the available experimental data. In any case the primary step involves a reaction at a non-activated C−H bond, which demonstrates the power of dioxiranes as oxygen transfer reagents.

Experimental Section

Materials and General Methods: NMR spectra were recorded with a Bruker DRX 400 and a Bruker DPX 200 spectrometer in $CDCl_3$ as solvent. IR spectra were obtained from KBr pellets or thin layers with a Perkin−Elmer 841 infrared spectrometer in the range from 400 to 4000 cm^{-1}. Mass spectra were recorded with a Varian MAT CH5 spectrometer at 70 eV. Experiments in organic glasses and kinetic measurements of the carbonyl oxide **1b** were performed with an Oxford Laboratory Cryostat (Variable Temperature Liquid Nitrogen Cryostat DN 1714). UV/Vis spectra were recorded using an HP 8452A diode array spectrophotometer at a resolution of 2 nm. Irradiations were carried out with Osram HBO 500 W mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation of the lamp was absorbed by a 10-cm path of water and by a Schott KG1 filter. For broad-band irradiation Schott cut-off filters were used (50% transmission at the wavelength specified), and for narrow-band irradiation interference filters in combination with dichroic mirrors and cut-off filters (420, 435, 455, 475 and 495 nm) were employed. The synthesis of diazomethane **6b** is outlined in Scheme 1.

(6-*tert*-Butyl-2,3,4-trimethylphenyl)phenylketimine Hydrochloride (16): In a 1-L three-necked flask equipped with a water separator, reflux condenser, and a dropping funnel 9.74 g (0.40 mol) of Mg turnings activated with iodine and 40 mL of dry diethyl ether were placed. Over a period of 90 min 50.04 g (0.20 mol) of 2-bromo-1-*tert*-butyl-3,4,5-trimethylbenzene (**15**) in 200 mL of dry diethyl ether and over a period of 1 h 8.6 mL (0.10 mol) of 1,2-dibromoethane in 50 mL of dry diethyl ether were aaded dropwise to the suspension. The mixture was heated under reflux for 3 h. A solution of 20.6 mL (0.20 mol) of benzonitrile in 300 mL of dry toluene was added dropwise in 90 min while the diethyl ether was removed using a water separator. The suspension was heated under reflux overnight. After cooling to room temperature, 150 mL of 7% HCl was added dropwise to the suspension. Concentrated HCl was added to dissolve all Mg. The resulting (6-*tert*-butyl-2,3,4-trimethylphenyl)phenylketimine hydrochloride (**16**) was separated by filtration as a colorless solid and used in the next step without further purification.

(6-*tert*-Butyl-2,3,4-trimethylphenyl)phenylketimine (17): The resulting (6-*tert*-butyl-2,3,4-trimethylphenyl)phenylketimine hydrochloride (**16**) was stirred in 200 mL of 10% NaOH. The solid was separated with a glass filter and washed with water until the water became neutral. After drying in vacuo, 27.31 g (0.1 mol; 50%) of (6-*tert*-butyl-2,3,4-trimethylphenyl)phenylketimine (**17**)was obtained. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.21 (s, 9 H, *tert*-butyl-CH_3), 1.95 (s, 3 H, Me-CH_3), 2.16 (s, 3 H, Me-CH_3), 3.34 (s, 3 H, Me-CH_3), 7.21−7.41 (m, $H_{aromat.}$) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.58, 17.63, 21.15, 32.75 (*tert*-butyl-CH_3), 36.09 (*tert*-butyl-C_{quat}), 126.83, 128.16, 128.35, 130.71, 133.18, 133.39, 136.02, 136.83, 139.30, 143.72, 180.80 (C=N−) ppm. IR (KBr): $\tilde{\nu}$ = 3441, 3274, 3014, 2964, 2870, 1738, 1608, 1575, 1485, 1449, 1396, 1361, 1350, 1300, 1286, 1257, 1210, 1189, 1161, 1153, 1074, 1029, 1002, 976, 935, 920, 891, 869, 789, 767, 736, 701, 689, 670 cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 278 (18) [M^+], 262 (42), 247 (38), 222 (6), 186 (5), 172 (4), 115 (4), 104 (10), 91 (8), 77 (11), 51 (5), 41 (8), 29 (5).

(6-*tert*-Butyl-2,3,4-trimethylphenyl)phenyldiazomethane (6b): The procedure described by Zimmerman and Paskovich[40] for the synthesis of dimesityldiazomethane (**6a**) was adapted for the synthesis of **6b**. N_2O_4 was condensed at −20 °C into a flask containing 10 g of anhydrous sodium acetate and 40 mL of dry CCl_4. A solution of 10.0 g (0.036 mol) of (6-*tert*-butyl-2,3,4-trimethylphenyl)phenylketimine (**17**) in 120 mL of dry CCl_4 was added dropwise at 0 °C within 20 min. The deep purple mixture was stirred at 0−5 °C for 1 h and subsequently poured into ice/water. The organic layer was washed two times with a saturated Na_2CO_3 solution and one time with water. After drying with $MgSO_4$ and filtration, the solution was concentrated in a rotary evaporator. The *N*-nitroso(6-*tert*-butyl-2,3,4-trimethylphenyl)phenylketimine (**18**) was used directly for the next step without further purification. The nitroso compound **18** was dissolved in 70 mL of dry diethyl ether and at −40 °C under argon added dropwise to a mixture of 0.91 g (0.024 mol) of $LiAlH_4$ in 40 mL of dry diethyl ether. The suspension was stirred at 0 °C for 30 min. The temperature was maintained at −20 °C and 30 mL of dry methanol was added. After warming to 0 °C, 30 mL of water was added. After filtration, the organic layer was washed two times with water and dried with $MgSO_4$. Removal of the solvent in vacuo resulted in a red-purple oil that was dissolved in *tert*-butyl methyl ether and chromatograpically purified [Al_2O_3 (neutral), *tert*-butyl methyl ether]. After drying with $MgSO_4$ and removal of the solvent, 4.33 g (0.015 mol; 41%) of purple (6-*tert*-butyl-2,3,4-trimethylphenyl)phenyldiazomethane (**6b**) was obtained. The diazo compound **6b** was further purified by preparative-scale HPLC (RP-18, methanol). M.p. 128 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 9 H, *tert*-butyl-CH_3), 2.18 (s, 3 H, *ortho*-CH_3), 2.23 (s, 3 H, *meta*-CH_3), 2.37 (s, 3 H, *para*-CH_3), 7.27 (s, 1 H, aromat.), 6.99−7.03 (t), 7.25−7.29 (m) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.14 (*meta*-CH_3), 17.20 (*ortho*-CH_3), 21.29 (*para*-CH_3), 31.89 (*tert*-butyl-CH_3), 36.29 (*tert*-butyl-C_{quat}), 59.40(C=N_2), 121.74, 122.59 (*ipso*-C), 123.36, 126.94, 128.91, 133.75 (*meta*-C), 137.90 (*para*-C), 140.14 (*ortho*-C, CH_3), 149.27 (*ortho*-C, *tert*-butyl-CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2964 (s), 2343 (vs), 2334 (vs), 2322 (s), 2046 (w), 1757 (m), 1746 (m), 1670 (m), 1599 (m), 1573 (s), 1486 (m), 1450 (s), 1385 (m), 1366 (m), 1349 (m), 1315 (m), 1277 (m), 1196 (m), 1160 (m), 1074 (m), 1028 (m), 1001 (m), 934 (m), 872 (m), 818 (m), 789 (s), 742 (m), 701(m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 264 (17) [$M^+ - N_2$], 249 (100), 234 (17), 219 (13), 192 (5), 178 (5), 171 (24), 157 (8), 143 (8), 129 (43), 105 (8), 91 (25), 77 (6), 41 (7), 28 (19). HRMS: calcd. 292.194; found 292.193949. $C_{20}H_{24}N_2$ (292.4): calcd. C 82.1, H 8.3, N 9.6; found C 81.85, H 8.51, N 9.49.

Phenyl 6-*tert*-Butyl-2,3,4-trimethylbenzoate (5b): 1.56 g (0.007 mol) of 6-*tert*-butyl-2,3,4-trimethylbenzoic acid, 0.67 g (0.007 mol) of phenol and 9.03 g (0.043 mol) of trifluoroacetic anhydrid were heated under an argon for 24 h. The brown oil was washed with water and diluted NaOH solution. The organic layer was dried with $MgSO_4$, filtered and the solvent was removed. The ester **5b** was obtained as a colourless solid: 0.231 g (0.67 mol; 11%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.45 (s, 9 H, *tert*-butyl-CH_3), 2.19 (s, 3 H, *meta*-CH_3), 2.31 (s, 3 H, *para*-CH_3), 2.35 (s, 3 H, *ortho*-CH_3), 7.17 (s, 1 H, aromat.), 7.26−7.30 (m), 7.41−7.63 (m) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.39 (*meta*-CH_3), 17.36 (*ortho*-CH_3), 21.18 (*para*-CH_3), 32.49 (*tert*-butyl-CH_3), 35.76 (*tert*-butyl-$C_{quat.}$), 121.35, 125.91, 126.13, 129.55, 130.30 (*ortho*-C, -CH_3), 133.44

(*meta*-C), 137.52 (*para*-C), 143.46 (*ortho*-C, *tert*-butyl-CH_3), 150.92, 170.60 (COO) ppm. MS (EI, 70 eV): *m*/*z* (%) = 296 (0.33) [M^+], 281 (0.5), 256 (0.5), 203 (100), 161 (12), 145 (5), 133 (8), 119 (6), 105 (5), 91 (5), 84 (8), 65 (5), 55 (8), 41 (5).

(6-*tert*-Butyl-2,3,4-trimethylphenyl) Phenyl Ketone (3b): 0.134 g of diazomethane **2b** in 60 mL of CCl_3F was placed in a cuvette cooled to −20 °C. The solution was purged with oxygen and irradiated with a high-pressure mercury arc lamp. The ketone **3b** was isolated from the reaction mixture by preparative HPLC (RP-18; methanol/water, 85:15) as a colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (s, 9 H, *tert*-butyl-CH_3), 1.90 (s, 3 H, *ortho*-CH_3), 2.14 (s, 3 H, *meta*-CH_3), 2.33 (s, 3 H, *para*-CH_3), 7.19 (s, 1 H, aromat.), 7.40−7.42 (m), 7.43−7.53 (m) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.17 (*meta*-CH_3), 17.56 (*ortho*-CH_3), 21.16 (*para*-CH_3), 32.53 (*tert*-butyl-CH_3), 35.94 (*tert*-butyl-$C_{quat.}$), 126.50, 128.58, 132.49 (*ortho*-C, -CH_3), 133.00 (*meta*-C), 136.00 (*ipso*-C), 136.49 (*para*-C), 144.24 (*ortho*-C, *tert*-butyl-CH_3), 202.39 (CO) ppm. MS: *m*/*z* = 280 [M^+], 265, 250, 203, 128, 115, 105, 77, 51.

Synthesis of Carbonyl Oxide 1b in Solution or in an Organic Glass: A solution of 3 mg of **6b** in 6 mL of $CFCl_3/CF_2BrCF_2Br$ (1:1) was purged with oxygen for 15 min and cooled to 185 K for solution experiments in the Oxford cryostat or to 78 K to form an organic glass. The carbonyl oxide **1b** was generated by irradiation of the solution or glass with a high-pressure mercury arc lamp in combination with cut-off filters (λ > 515 nm or 495 nm). The formation and thermal decay of **1b** was monitored by UV/Vis spectroscopy.

Synthesis of Dioxirane 2b in Solution: For the small-scale synthesis of dioxirane **2b** a solution of **6b** in $CFCl_3/CF_2BrCF_2Br$ (1:1) was purged with oxygen and irradiated with λ > 495 nm at −60 °C. The reaction was monitored by analytical HPLC (RP-18, methanol). For the preparative-scale synthesis of **2b** a specially designed photoreactor with a 150-W Hg/Cd medium-pressure arc lamp (Heraeus-Nobelight TQ 150 Z3) was used (Figure 4). The filtering solution with 50% transmission at 435 nm contained 43.88 g of $CuCl_2 \times 2\ H_2O$, 600 mL of water and 115 mL of concentrated aqueous HCl. The flask was filled with 300 mL of $CFCl_3$ and purged with O_2 for 10 min. The photolysis was performed at −78 °C under O_2 purging. To prevent the reaction of carbonyl oxide **1b** with excess of the diazo compound **6b** to give ketone **3b**, a solution of 100−150 mg of **6b** in 20 mL CCl_3F was added in small portions during the photolysis. The reaction was monitored by analytical HPLC (RP-18, methanol). After the consumption of **6b**, the solvent was evaporated in vacuo at low temperature (−50 to −20 °C).

Isolation of Dioxirane 2b and the Byproducts: The photolysis mixtures from the photolysis in the photo reactor were collected and separated by preparative HPLC (Si60-10CN column, 20 cm; *tert*-butyl methyl ether/pentene, 1:100 as eluent). The column was cooled to −20 °C and the dioxirane fraction was collected in a brown flask cooled by dry ice and purged with argon.

(6-*tert*-Butyl-2,3,4-trimethylphenyl)phenyldioxirane (2b): ^{1}H NMR (400 MHz, $CDCl_3$, − 20 °C): δ = 1.24 (s, 9 H, *tert*-butyl-CH_3), 2.01 (s, 3 H, *ortho*-CH_3), 2.14 (s, 3 H, *meta*-CH_3), 2.32 (s, 3 H, *para*-CH_3), 7.25 (s, 1 H, aromat.), 7.26−7.35 (m) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, −20 °C): δ = 15.46 (*meta*-CH_3), 18.57 (*ortho*-CH_3), 21.42 (*para*-CH_3), 33.18 (*tert*-butyl-CH_3), 36.20 (*tert*-bButyl-$C_{quat.}$), 127.34, 127.63, 135.00 (*meta*-C), 137.24 (*para*-C), 145.58 (*ortho*-C, *tert*-butyl-CH_3) ppm.

4,4,6,7,8-Pentamethyl-1-phenylisochroman-1-ol (11): Colourless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 3 H, -CH_3), 1.34 (s, 3 H, -CH_3), 1.87 (s, 3 H, *ortho*-CH_3), 2.06 (s, 3 H, *meta*-CH_3), 2.31 (s, 3 H, *para*-CH_3), 3.20 (s, 1 H, OH), 3.48/3.50 (d, 1 H, *J* = 11.0 Hz), 3.91/3.94 (d, *J* = 11.0 Hz, 1 H), 6.89 (s, 1 H, aromat.), 7.27−7.34 (m, 5 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.62 (*meta*-CH_3), 17.98 (*ortho*-CH_3), 21.14 (*para*-CH_3), 25.96 (−CH_3), 28.41 (−CH_3), 33.64 ($C_{quat.}$), 70.44 (CH_2), 98.20 (semiacetal-C), 124.36, 125.81, 127.64, 128.04, 132.48 (*ipso*-C), 134.82 (*ortho*-C, -CH_3), 135.13 (*meta*-C), 136.92 (*para*-C), 141.94, 144.81 (*ipso*-C) ppm. IR (KBr): $\tilde{\nu}$ = 3394 (vs, OH), 2952 (s), 2868 (m), 1601 (w), 1449 (s, *tert*-butyl), 1388 (m), 1356 (m), 1309 (w), 1207 (s), 1172 (s), 1075 (m), 1025 (s), 1000 (m), 978 (m), 964 (m), 896 (m), 867 (m), 832 (m), 758 (s), 699 (s), 619 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 296 (18) [M^+], 279 (8), 265 (15), 250 (7), 235 (8), 219 (100), 201 (20), 189 (5), 173 (6), 161 (14), 143 (5), 118 (8), 105 (30), 77 (22), 65 (4), 51 (5), 43 (7), 28 (7).

1,1,4,5,6-Pentamethyl-3-phenylindan: Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (s, 3 H, -CH_3), 1.24 (s, 3 H, -CH_3), 1.83 (s, 3 H, *ortho*-CH_3), 1.87−1.92 (dd, 1 H, *J* = 6.02, *J* = 8.53 Hz), 2.13 (s, 3 H, *meta*-CH_3), 2.33 (s, 3 H, *para*-CH_3), 2.47−2.50 (dd, 1 H, *J* = 9.03, *J* = 13.06 Hz), 4.42−4.46 (dd, 1 H, *J* = 6.03, *J* = 12.8 Hz), 6.89 (s, 1 H, aromat.), 7.05−7.08 (m, 2 H), 7.13- 7.17 (m, 1 H), 7.21−7.26 (2 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.28 (*meta*-CH_3), 16.89 (*ortho*-CH_3), 21.18 (*para*-CH_3), 30.04 (−CH_3), 30.35 (−CH_3), 43.36, 48.81 (−CH), 52.55 (−CH_2), 121.09, 125.59, 127.72, 128.29, 133.35 (*meta*-C), 133.55 (*ortho*-C, -CH_3), 135.71 (*para*-C), 140.20 (*ipso*-C), 147.26 (*ipso*-C), 150.51 ppm. MS: *m*/*z* = 264 [M^+], 249, 234, 219, 201, 171, 156, 141, 129, 115, 91, 78, 51.

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