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On the decarboxylation of 2-methyl-1-tetralone-2-carboxylic acid – oxidation of the enol intermediate by triplet oxygen†

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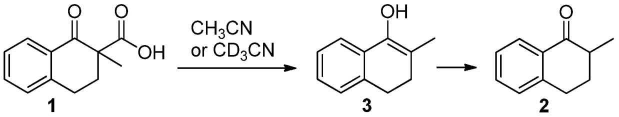
The formation of 2-methyl-1-tetralone from the metal-free and base-free decarboxylation of 2-methyl-1-tetralone-2-carboxylic acid involves 2-methyl-3,4-dihydro-1-naphthol as an intermediate. The reaction of this enol with atmospheric oxygen leads to 2-hydroperoxy-2-methyl-1-tetralone. The oxidation mechanism is confirmed by quantum chemical calculations at the (U)B3LYP/6-31G(d) level of theory.

In 1997, we reported that the decarboxylation of 2-methyl-1-tetralone-2-carboxylic acid **1** in the presence of a chiral amino alcohol affords enantioenriched 2-methyl-1-tetralone **2**.[1] Monitoring, using UV and ^{1}H NMR spectroscopies, the transformation of **1** in the absence of any additive led us, in 2004, to assign 2-methyl-3,4-dihydro-1-naphthol (**3**) as an intermediate leading to **2** (Scheme 1).[2]

In 2008, Baiker *et al.* reinvestigated the additive-free decarboxylation of **1**.[3,4] They were able to reproduce our UV experiments but not those concerning the NMR analyses.[4] They, however, attributed the evolution of the UV spectrum with time to an oscillation reaction rather than to the sequence shown in Scheme 1.[4] According to them, "no reliable indication of the formation of an enolic intermediate could be obtained by spectroscopic methods".[4]

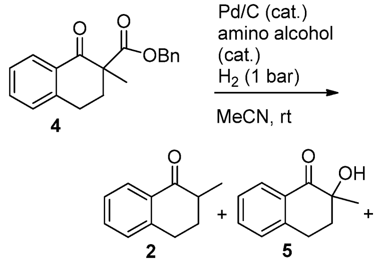


Scheme 1 Decarboxylation of 2-methyl-1-tetralone-2-carboxylic acid **1** involving the formation of enol **3**.

Optically active **2** can also be attained from the Pd-catalyzed hydrogenolysis of 2-methyl-1-tetralone-2-carboxylic acid benzyl ester (**4**) in the presence of chiral aminoalcohols.[5] Repeating this hydrogenolysis, Baiker *et al.* have, besides **2**, isolated small amounts of 2-hydroxy-2-methyl-1-tetralone (**5**) and 2-methyl-1-tetralol (**6**) (Scheme 2).[4] They assumed that the Pd-catalyzed debenzylation produces the ketoacid **1**,[3,4] and suggested the formation of **5** from the reaction of **2** with traces of oxygen, and that of **6** from the reduction of **2**.[4]

These two reports of Baiker prompted us to revisit the ^{1}H NMR monitoring of the decarboxylation of **1** and to investigate its reactivity under an oxygen atmosphere.

We have to point out that we attributed the structure of the intermediate, which leads to **2** from **1**, from the comparison of its spectroscopic characteristics with those of 2-methylinden-3-ol obtained from the Norrish type II photoreaction of 2-methyl-2-isobutyl-1-indanone.[6] This photo-enol was identified from its ^{1}H NMR (methyl group as a singlet) and UV (λ_{max}: 265–270 nm)[7] characteristics, and its quantitative tautomerisation into



Scheme 2 Palladium catalysed transformation of keto ester **4**.

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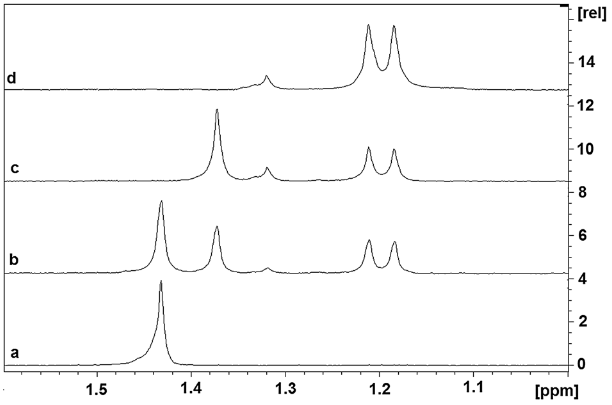
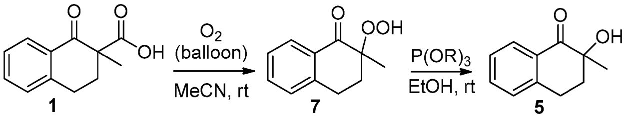
2-methyl-1-indanone. Consequently, the structure **3** agreed with the ^{1}H NMR (a singlet at 1.37 ppm) and UV ($\lambda_{\max}$: 280 nm) spectra obtained from the monitoring of the decomposition of **1**. Moreover, both ^{1}H NMR and UV monitoring showed that this unstable compound evolved in the formation of **2**.

After several attempts, we found that the problem of the ^{1}H NMR reproducibility apparently resulted from the crystallization procedure of the substrate sample. We suspect that traces of an undetermined compound can favor either the stability of the enol, or its tautomerisation into the ketone. Indeed, we obtained erratic NMR spectra when **1** was isolated according to the Baiker procedure, whereas reproducible results, similar to those reported previously,[2] were issued for samples of **1** isolated as described in the experimental part.† Such samples are relatively stable at room temperature, the decarboxylation occurring slowly. A part of a new ^{1}H NMR spectrum of a solution of **1** (1.5 mg) in CD_3CN (0.8 mL) is depicted in Scheme 3, curve a, the singlet (δ = 1.44 ppm) corresponding to the methyl substituent.[1,3,4] After 24 h at rt and then 1 h at 45 °C, this sample led to the NMR spectrum depicted in Scheme 3, curve b, which shows two new signals: a singlet at 1.37 ppm and a doublet at 1.20 ppm (J = 6.7 Hz), the doublet corresponding to the methyl of **2**,[3,4,8] whereas the singlet is attributed to the methyl of **3**.[1,6] An additional reaction time of 96 h at rt followed by 10 min at 45 °C led to the disappearance of the signal at 1.44 ppm, indicating the complete consumption of **1** (Scheme 3, curve c). This was accompanied by the increase in the signals at 1.37 and 1.20 ppm, the singlet disappearing at the profit of the doublet when the reaction time was prolonged to 14 days at rt (Scheme 3, curve d). These results agree with the reaction cascade shown in Scheme 1, and also with the usually accepted cyclic, six-center mechanism of the decarboxylation of β-ketoacids.[9]

The NMR spectra of the decarboxylation of **1** show a weak singlet at 1.32 ppm (Scheme 3, curves b–d), which could correspond to the methyl of an oxygenated compound, *i.e.* **5** or 2-hydroperoxy-2-methyl-1-tetralone **7**. This led us to examine the reaction of **1** in MeCN under an oxygen atmosphere. Interestingly, **7** was isolated in 78% yield, its reduction with $P(OEt)_3$[10] provided, in a few minutes, the α-ketol **5** (Scheme 4). Similar peroxides were reported in the silyl enol ethers with singlet oxygen.[11] In contrast, an acetonitrile solution of **2** under the same experimental conditions did not afford **7**. Thus, this oxidation concerned an intermediate obtained from **1** and not from **2**.



Scheme 3 NMR spectra of the decarboxylation process of 2-methyl-1-tetralone-2-carboxylic acid **1**.



Scheme 4 Formation of the hydroperoxide **7** induced by decarboxylation of 2-methyl-1-tetralone-2-carboxylic acid **1**.

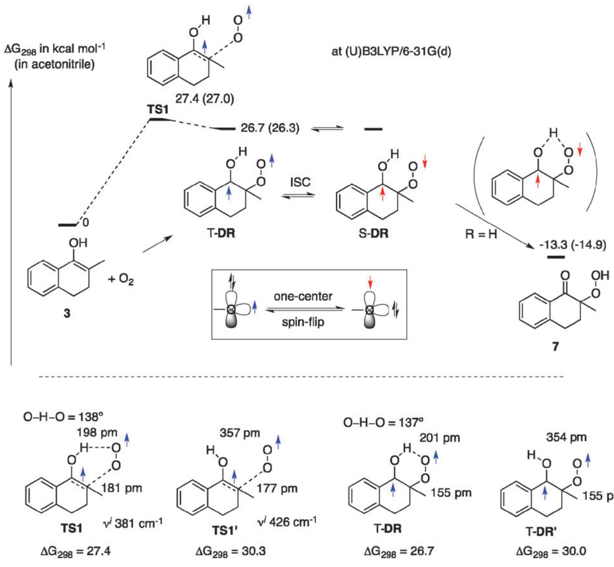
The ^{1}H NMR spectrum of **5** agrees with that provided in the literature,[4,12] and the mass spectrum corresponds to this structure. Surprisingly, the ^{1}H NMR signals of the methyl group of **5** (δ = 1.40 ppm) and **7** (δ = 1.48 ppm) in $CDCl_3$ disagree with our above proposal on the meaning of the singlet at 1.32 ppm in the spectra in Scheme 3. Actually, the ^{1}H NMR spectra of **5** and **7** depend on the solvent, the above signal of **5** and **7** in CD_3CN being at 1.32 ppm and 1.37 ppm, respectively. Consequently, traces of **5** were obtained from **1** under the conditions leading to the spectra depicted in Scheme 3. Given these results, we examined the stability of **7**: at rt in MeCN, its slow transformation into **5** has been observed. Thus, low amounts of **7** could be formed when monitoring the decarboxylation of **1**, their presence would not be detected from the spectra b and c in Scheme 3, because the signal of the corresponding Me group would be very small and hidden under that of **3**.

Procedures for the synthesis of compounds such as **5** and **7** are known. Basic conditions with oxygen and trialkyl phosphites provide **5** from **2**.[12,13] A radical reaction was suspected by Sajiki's team for the synthesis of 2-hydroxy-2-methyl-1-indanone from 2-methyl-1-indanone using oxygen, Pd/C as the catalyst and triethylamine in ethanol at room temperature.[14] Under these conditions, the formation of 2-hydroperoxy-2-methyl-1-indanone[15] and its reduction with the Pd/C–NEt_3 system is conceivable.[16] The recent procedure of Ritter uses the dinuclear Pd^{II} complex $Pd_2(hpp)_2$, to catalyze the α-hydroxylation of **2** with oxygen, leading to **5** in 91% yield.[17] The corresponding mechanism remains unknown; it was speculated "that enol formation is important for hydroxylation".[17] From experiments and meticulous analysis, it appeared that this reaction has no radical character and that 2-hydroperoxy-2-methyl-1-tetralone is not an intermediate.[17] These literature reports do not give elements allowing explanation of the formation of an oxidation compound from **1** and not from **2** under both base-free and palladium-free conditions. This leads us to assume that **7** is produced from **3**. Actually, the formation of α-hydroperoxy ketones from the reaction of enols with atmospheric oxygen in the absence of any additive has already been reported.[18] As compound **3** possesses a styrene moiety, it should also be mentioned that triplet oxygen may be added to styrene which plays a role in the polymerization under RAFT conditions of this monomer.[19]

Doubts about the oxidation of enols with atmospheric oxygen may originate from a lack of mechanistic understanding although the transformation was observed in the past[18] and it has also been reported in recent literature.[20] In neutral and aprotic media and in contrast to enolates,[21] electron transfer from the enols such as **3** or the corresponding enolalkylethers to triplet oxygen ($^3O_2$) is hardly possible.[22] Furthermore, the generation of singlet oxygen ($^1O_2$) is not possible under the dark reaction conditions in the absence of a sensitizer (Scheme 4). *Via* calculations, we checked whether the direct addition of triplet oxygen to **3** may occur.

Quantum chemical calculations for the oxidation reaction were performed at the (U)B3LYP/6-31G(d) level of theory[23] with the Gaussian 09 suite of program (Scheme 5).[24] The transition state **TS1** (R=H), ΔG_{rel} = 27.4 kcal mol^{-1}, with an imaginary frequency (ν^i) of 381 cm^{-1} and S^2 = 2.03 was found in the addition reaction of the enol **3** (R=H) with $^3O_2$ to give the triplet diradical T-**DR** (S^2 = 2.03), ΔG_{rel} = 26.7 kcal mol^{-1}. The intramolecular hydrogen-bonding stabilization interactions were found in **TS1** and T-**DR**. Thus, the atom distance between the peroxy oxygen and hydrogen of OH was calculated to be 198 pm and 201 pm as shown in the structures **TS1** and T-**DR**, respectively. The O–H–O angles in **TS1** and T-**DR** were found to be 138° and 137°, respectively. The calculated atom-distances and angles suggest that the hydrogen-bonding interactions are categorized into the "moderate hydrogen bonds".[25] Indeed, the non-hydrogen bonded structures **TS1**′ (S^2 = 2.04) and T-**DR**′ (S^2 = 2.03) were found to be less stable than the hydrogen-bonded ones **TS1** and T-**DR** by 2.9 and 3.3 kcal mol^{-1}, respectively.

The optimization of the singlet state of S-**DR** from the hydrogen-bonded structure of T-**DR** at the broken-symmetry (BS)[26]-UB3LYP/6-31G(d) level of theory finally gave the hydroperoxide **7** as an equilibrated structure. Thus, the hydrogen-bonded singlet diradical S-**DR** was not found as an equilibrated structure, suggesting that the hydrogen transfer process is a barrierless process in S-**DR**. Actually, a non-hydrogen-bonded structure of the singlet diradical S-**DR**′ (S^2 = 0.86, ΔG_{rel} = 29.9 kcal mol^{-1}) was found as an equilibrated structure at the BS-UB3LYP/6-31G(d) level of theory. The singlet–triplet energy gap in **DR**′ was, thus, nearly negligible.



Scheme 5 Quantum chemical calculations upon the addition of triplet oxygen ($^3O_2$) to enol **3** forming 2-methyltetralone.

The intersystem crossing (ISC) process from T-**DR** to S-**DR** is key for the formation of the hydroperoxide **7**. For such a diradical with the short distance of the two radical sites, the rate of the ISC process is directly related to the magnitude of spin–orbit coupling (SOC). Strong SOC for two-center interactions is proposed to be favored by the following factors: (1) if the angle of the axes of the two radical orbitals is close to 90°; (2) for "ionic" admixture in the singlet state wave function; and (3) for special proximity of the two radical orbitals.[27] However, the process is spin-forbidden, thus, the lifetime of the triplet diradicals is in general microsecond time scale at room temperature. For diradicals including oxy radicals such as T-**DR**, in which one-center spin-flip on oxygen is possible (Scheme 5), Minaev and coworkers found that the one-center spin–orbit interaction effectively proceeds from the triplet state to the singlet state.[28] Thus, the ISC process from T-**DR** to S-**DR** would be a fast process to give the hydroperoxide **7**. All the computational results clearly indicate that the hydroperoxide formation is possible in the reaction of **3** with $^3O_2$. The fast ISC process and the spontaneous hydrogen transfer in S-**DR** are the key for the oxidation reaction.

A small solvent effect was computed at the same level of theory in the reaction profile of the oxidation of **3** (Scheme 5). Thus, the energy barrier of the reaction of $^3O_2$ with **3** was calculated to be 27.0 kcal mol^{-1} in acetonitrile, for which Polarized Continuum Model (PCM)[29] was used for estimating the solvent effect. This value is nearly the same as 27.4 kcal mol^{-1} obtained in the calculation without the solvent.

The additive-free decarboxylation of 2-methyl-1-tetralone-2-carboxylic acid in acetonitrile involves the formation of 3,4-dihydro-2-methylnaphthalen-1-ol as an intermediate leading to 2-methyl-1-tetralone. In the presence of oxygen, the decarboxylation of this ketoacid under base-free and metal-free conditions leads to 2-hydroperoxy-2-methyl-1-tetralone through, most likely, the oxidation of the enol intermediate. Calculations revealed that triplet oxygen may be directly added to 3,4-dihydro-2-methylnaphthalen-1-ol. A previous electron transfer from the enol to triplet oxygen followed by charge combination is not necessary. Under the reaction conditions such a redox process would be endothermic.

Experimental section

2-Methyl-1-tetralone-2-carboxylic acid (1)

A solution of 2-carboethoxy-2-methyl-1-tetralone (710 mg, 3.05 mmol) in H_2O–MeOH (1 : 3, 6 mL) was added to a solution of KOH (550 mg, 9.80 mmol) in H_2O–MeOH (1 : 3, 14 mL). The mixture was stirred at room temperature under air for 24 h. After addition of CH_2Cl_2 (30 mL), the recovered aqueous phase was acidified using 2 M HCl, then extracted with CH_2Cl_2

(3 × 10 mL). The organic layer was washed with brine, dried over $MgSO_4$, and then evaporated to dryness. The resulting crude solid was recrystallized in light petroleum ether leading to white crystals of **1** (209 mg, 40% yield); its ^1H NMR characteristics were in agreement with those reported.[1,3,4] The acid was stored in the freezer.

^1H NMR studies. An ^1H NMR tube was charged with **1** (1.5 mg) and CD_3CN (0.8 mL) under an air atmosphere. After dissolution of **1** by shaking at room temperature, its ^1H NMR spectrum was immediately recorded with a Bruker Avance DRX 250 apparatus employing tetramethylsilane as internal reference. Then, the decarboxylation was monitored as described in the text.

2-Hydroperoxy-2-methyl-1-tetralone (7)[30]

A solution of **1** (30 mg, 0.15 mmol) in MeCN (15 mL) was stirred at room temperature under oxygen (balloon) for 129 h. Filtration of the mixture over silica gel (petroleum ether/ethyl acetate: 70/30) afforded 2-hydroperoxy-2-methyl-1-tetralone (22 mg, 78% yield).

2-Hydroxy-2-methyl-1-tetralone (5)

A solution of **7** (30 mg, 0.15 mmol) and $P(OEt)_3$ (32 µl, 0.19 mmol) in PhMe (2 mL) was stirred at room temperature for 5 min. Purification of the mixture over silica gel (petroleum ether/ethyl acetate: 70/30) afforded 2-hydroxy-2-methyl-1-tetralone (16 mg, 60% yield).

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