UV-Laser Photochemistry: Trapping of the Norrish Type II Triplet Diradical 1-Hydroxy-4-methyl-1-phenyl-1,4-pentanediyl with Molecular Oxygen

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The triplet lifetime ($^3\tau$ = 131 ± 5 ns) of diradical **2**, produced in the laser photolysis (334 nm) of 4-methyl-1-phenyl-1-pentanone (**1**) in methanol, was determined by dioxygen trapping. This lifetime agrees well with the value determined by laser flash photolysis ($^3\tau$ = 97 ns), thereby establishing the reliability of the trapping technique. The trapping product was prepared by independent synthesis and chracterized as 3-hydroxy-1,2-dioxolane **9**, the ring tautomer of hydroperoxide **6**.

UV-Laserphotochemie: Abfang des Norrish-Typ-II-Triplett-Diradikals 1-Hydroxy-4-methyl-1-phenyl-1,4-pentandiyl mit molekularem Sauerstoff

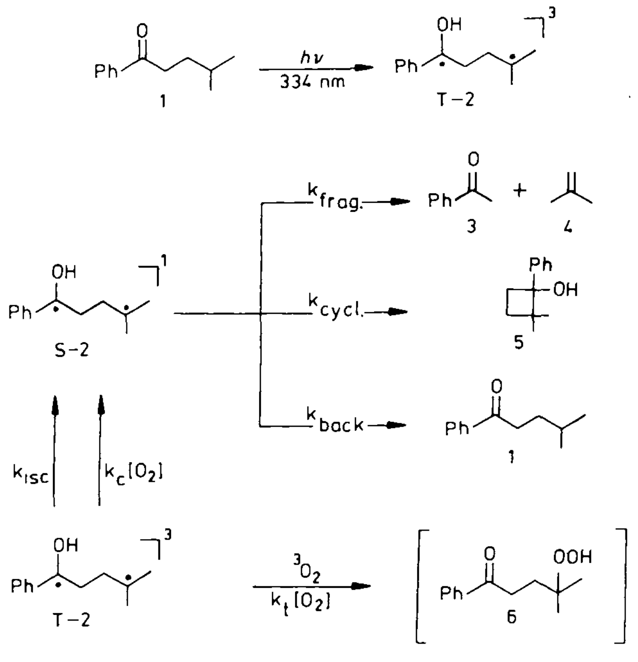
Die Lebensdauer des Triplett-Diradikals **2** ($^3\tau$ = 131 ± 5 ns), erzeugt durch Laserphotolyse (334 nm) von 4-Methyl-1-phenyl-1-pentanon (**1**) in Methanol, wurde durch Abfang mit molekularem Sauerstoff bestimmt. Diese Lebensdauer stimmt mit dem durch Laserblitzphotolyse erhaltenen Wert ($^3\tau$ = 97 ns) gut überein und belegt damit die Verläßlichkeit der Sauerstoff-Abfangtechnik. Das Abfangprodukt wurde durch eine unabhängige Synthese dargestellt und als 3-Hydroxy-1,2-dioxolan **9** identifiziert, das Ringtautomer des Hydroperoxids **6**.

The chemistry of Norrish Type II diradicals is well established[1)], and recently spectral characterization and lifetime measurements have become available[2)] on these important photochemical reaction intermediates. Molecular oxygen readily reacts with such triplet 1,4-diradicals, and we decided to undertake a quantitative study of the dioxygen trapping of the 1-hydroxy-4-methyl-1-phenyl-1,4-pentanediyl (**2**) obtained in the irradiation of 4-methyl-1-phenyl-1-pentanone (**1**)[3)]. The reason for this was that the lifetime of this triplet diradical has been determined by time-resolved laser flash photolysis[4a)] and photoacoustic calorimetry[4b)], so that comparison of these lifetimes with that acquired by the dioxygen trapping technique[5)] would provide a rigorous test of the validity and reliability of the latter method. Of particular significance is the fact that in the laser flash studies the rate constant for dioxygen trapping, which is essential in the determination of triplet lifetimes by the trapping technique, are directly accessible.

In Scheme 1 the photochemistry of the Norrish Type II reaction for ketone **1** is summarized. Application of steady-state kinetics allows to derive the trapping expression given in eq. (1)[6)], which relates the mole fraction of trapping product (x_P), in this case peroxides, to the triplet lifetime ($^3\tau$). Crucial in this Scheme is suppression of the back-reaction of the Norrish Type II diradical **2** to starting ketone **1** (k_{back} in Scheme 1). Fortunately, in methanol this condition obtains rigorously, since the sum of the quantum yields for fragmentation and for cyclization are nearly unity[7)].

The results of the quantitative trapping experiments for the triplet diradical **2** with molecular oxygen in methanol are given in Table 1 and a typical trapping plot exhibited in Figure 1. The agreement of the triplet lifetime measured by dioxygen trapping ($^3\tau$ = 131 + 5 ns) with that reported

Scheme 1



$$\frac{1}{x_P} = \frac{1}{1-x_H} = \frac{1}{T_f} + \frac{1}{k_t\cdot{}^3\tau\cdot[O_2]} \qquad (1)$$

x_P = mole fraction of peroxide (trapped product); x_H = mole fraction of hydrocarbons (untrapped product); $T_f = k_t/(k_t + k_c)$ is the trapping factor; k_t = rate constant for oxygen trapping; k_c = rate constant for spin-catalyzed intersystem crossing; $^3\tau = 1/k_{ISC}$ is the triplet lifetime; k_{ISC} = rate constant for inherent intersystem crossing.

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by laser flash photolysis ($^3\tau$ = 97 ns) is most gratifying. Also, the trapping factors (T_f = 0.26) agree well within experimental error[3c]. It should be emphasized that the encounter of the triplet diradical **2** with triplet oxygen is diffusion-controlled and leads mainly (ca. 74%) to spin-catalyzed intersystem crossing rather than trapping (ca. 26%). Besides constituting a reliable method for estimating the lifetimes of triplet diradicals that are generated in photochemical reactions, the real advantage of the dioxygen trapping techniques is that spectroscopically "invisible" triplet diradicals (time-resolved laser flash photolysis requires a chromophore for detecting the transient!) can be monitored[5]. Consequently, the dioxygen trapping technique nicely complements the well established spectroscopic methods[4].

Table 1. Diradical lifetime and trapping factor of triplet diradical **2** obtained using the dioxygen trapping technique[a]

$(k_t\cdot{}^3\tau)^{-1}\cdot 10^3$ (slope, M)	T_f^{-1} (intercept)	r (corr. coef.)	T_f	$^3\tau$ [ns]
4.50 ± 0.154	3.81 ± 0.051	0.9897	0.26 ± 0.01	131 ± 5[b]

[a] Statistical errors given. — [b] $k(O_2) = k_t + k_c = 6.5\cdot10^9\ M^{-1}\ s^{-1}$, ref.[2b].

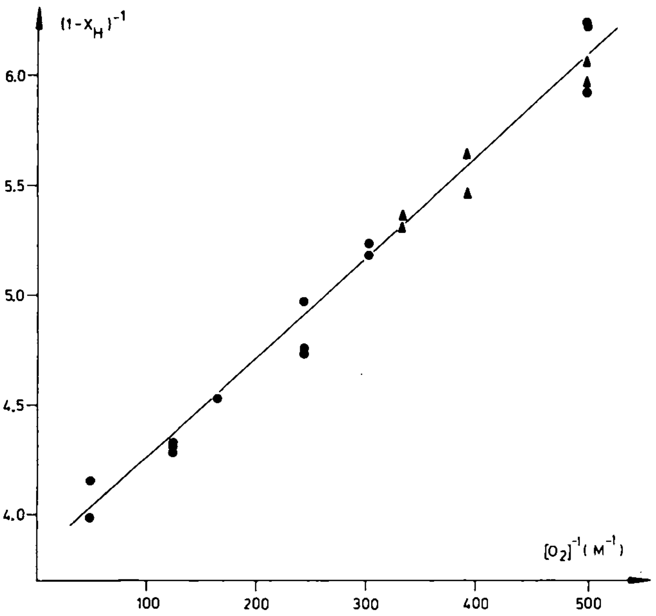
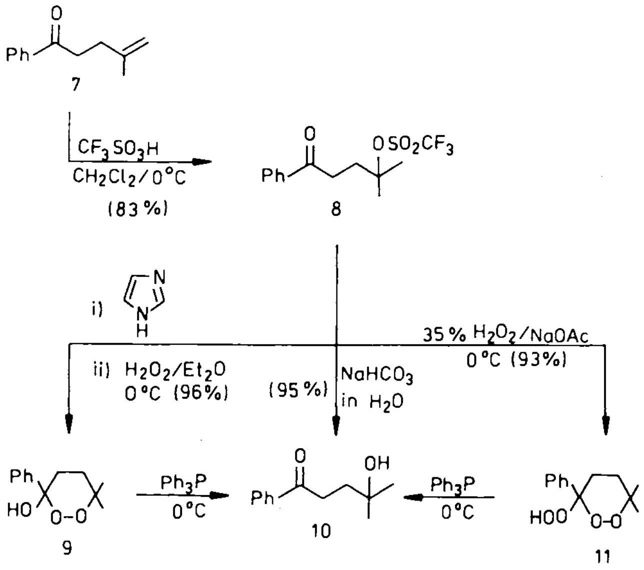


Figure 1. Double reciprocal plot of the trapping efficiency of triplet diradical **2** as a function of oxygen concentration in methanol (10°C); x_H = mole fraction of **3**, **4**, and **5**; sets A (●) and B (▲) refer to different concentrations of ketone **1**

An essential requisite for the dioxygen trapping technique, however, is that the peroxide products be definitively established as trapping and not as secondary products. To comply with this condition, the peroxide structure must be rigorously determined. Although the dioxygen trapping product of the diradical **2** was previously reported[3], its unambiguous characterization was still lacking. The difficulty arises from the fact that in the photolysis of ketone **1** even under 10 atm oxygen pressure too little peroxide product is formed to enable isolation, purification, and characterization. Furthermore, the peroxide is photolabile[3c]. Thus, an independent synthesis was sought, which is outlined in Scheme 2. Enone **7**[8] was first converted into the triflate **8** in 83% yield[9] and subsequently treated with imidazole[10]/hydrogen peroxide to afford the desired γ-hydroperoxy ketone **6** (cf. Scheme 1 for structure) in 96% yield. The latter spontaneously cyclizes to its ring tautomer **9**[11], as directly established be ^{1}H-NMR spectra of the reaction mixture. Peroxide **9** was isolated and rigorously characterized by spectral means as well as reduction with triphenylphosphine to the alcohol **10** in 95% yield. The latter was prepared in 95% yield by hydrolysis of the triflate **8**.

Scheme 2



Attempts to prepare the γ-hydroperoxide **6** (or its ring tautomer **9**) by acid-catalyzed addition of hydrogen peroxide directly to enone **7** led to a complex mixture of peroxides. Furthermore, reaction of the triflate **8** with hydrogen peroxide, buffered by sodium acetate, gave the hydroperoxide **11** in 93% yield. Reduction of the latter by triphenylphosphine gave again the alcohol **10**. Therefore, the reaction conditions must be controlled stringently to obtain the peroxide **9**. The presence of the latter as dioxygen trapping product of diradical **2** in the photolysis of ketone **1** was established by TLC comparison with the authentic material.

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Experimental

Melting points (uncorrected): Reichert Thermovar Apparatus. — Infrared spectra: Beckman Aculab 4. — ^{1}H NMR: Hitachi-Perkin-Elmer R-24B (60 MHz). Bruker WM 400 spectrometer (400 MHz). — ^{13}C NMR: Bruker WM 400 spectrometer (100.6

MHz). – Mass spectra: Varian MAT CH 7. – Elemental analyses: Carlo Erba Model 1106 Analyzer. – Thin-layer chromatography (TLC): Polygram SIL/UV (40 × 80 mm), Macherey-Nagel & Co. – Column chromatography: Silica gel 70–230 mesh ASTM (activity III, Merck). – Solvents were purified according to standard literature procedures. – Known compounds were either purchased from commercial suppliers or prepared according to published methods and purified to match reported physical data.

Photolyses were carried out in a Rayonet Model RP-100 (Southern New England Ultraviolet Co.) photochemical reactor at 300 nm or with a Coherent Supergraphite CR 18 argon ion laser fitted with a selected UV tube. The UV-laser lines were separated by means of an external quartz prism and the 334-nm line was used in all irradiations.

Capillary GC was performed on a Fractovap 4100 (Carlo Erba Co.); for preparative GC a Model 4200 (Carlo Erba Co.) was used. Compounds used for capillary GC calibrations were purified by preparative GC prior to use.

4-Methyl-1-phenyl-1-pentaneone (**1**)[12a] and 4-methyl-1-phenyl-4-pentene-1-one (**7**)[8] were prepared according to literature procedures. 2,2-Dimethyl-1-phenyl-1-cyclobutanol (**5**)[12b] was isolated from the photolysate of **1** by preparative GC, using a 3-m Carbowax column.

Lifetime Determination of Triplet **2**: The procedure for the diradical lifetime determination has previously been described[5]. The analyses of the photolysates were performed by capillary GC on a 50-m OV-101 column with injector and column temperature of 200 and 120 °C, respectively (N_2: 1.6 kp/cm^2). Calibration plots for ketone **1** and the photoproducts **3** and **5** were determined using *n*-dodecane as internal standard. Measurements of set A and B (Figure 1) correspond respectively to concentrations of 21.1 and 22.3 mmol/l for ketone **1** and 3.26 and 4.77 mmol/l for *n*-dodecane in methanol.

4-Methyl-1-phenyl-4-trifluoromethanesulfonyl-1-pentanone (**8**): A flame-dried 100-ml round-bottomed flask, equipped with a magnetic spin bar and dropping funnel, was charged under nitrogen with 5.00 g (28.7 mmol) of **7** in 30 ml of absolute methylene chloride. The solution was cooled to 0 °C, and 4.30 g (28.7 mmol) of trifluoromethanesulfonic acid was slowly added at this temp., and the resulting mixture was stirred for 1 h at 25 °C. After rotary evaporation of the solvent, the dark brown residue was washed under nitrogen with absolute ether and dried at 0.1 Torr, affording 7.75 g (83%) of triflate **8** as colorless powder. – ^{1}H NMR ($CDCl_3$, 60 MHz): δ = 1.83 (s, 6H, CH_3), 2.50 (t, *J* = 7 Hz, 2H, CH_2), 4.36 (t, *J* = 7 Hz, 2H, CH_2), 7.20–8.27 (m, 5H, aromatic H).

Since **8** is extremely sensitive towards moisture, no further characterization was attempted.

3-Hydroxy-6,6-dimethyl-3-phenyl-1,2-dioxolane (**9**): A flame-dried 100-ml round-bottomed flask, equipped with a magnetic spin bar and dropping funnel, was charged under nitrogen with 1.00 g (3.08 mmol) of **8** in 40 ml of absolute methylene chloride and 10 ml of absolute ether. To this solution 0.47 g (6.90 mmol) of imidazole was added at 25 °C, and the solution was stirred for 1 h at this temp. The mixture was then cooled to 0 °C, and under vigorous stirring 20 ml of a ca. 1.50 M solution of anhydrous hydrogen peroxide in ether (ca. 30 mmol) was added at once. The solution was allowed to warm up to room temp., stirred for ca. 12 h, and extracted with ether (4 × 50 ml). The combined organic layers were washed with satd. sodium chloride solution (3 × 25 ml) and dried with magnesium sulfate. After rotary evaporation, the yellowish oil was purified by flash chromatography on silica gel at –25 °C using methylene chloride as eluent, yielding 0.62 g (96%) of **9** as light yellow oil. – IR (neat): ν = 3500–3200 cm^{-1}, 3070, 3040, 2975, 1600, 1490, 1445, 1380, 1370, 1235, 1115, 1040, 1020, 865, 765, 700. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.36 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.76–1.87, 2.01–2.15, 2.36–2.45 (each m, 4H, CH_2CH_2), 7.24–7.54 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 28.1 (q, CH_3), 29.2 (q, CH_3), 37.4 (t, CH_2), 37.8 (t, CH_2), 84.6 (s, C-6), 113.8 (s, C-3), 125.9 (d), 127.8 (d), 140.7 (s). – MS (70 eV): *m/z* (%) = 174 (32), 159 (14), 105 (100).

$C_{12}H_{16}O_3$ (208.3)	Calcd.	C 69.21	H 7.74
	Found	C 69.45	H 7.51

4-Hydroxy-4-methyl-1-phenyl-1-pentanone (**10**) *by Hydrolysis of* **8**: A stirred solution of 0.500 g (2.87 mmol) of **7** in 10 ml of methylene chloride was cooled to 0 °C, and 0.430 g (2.87 mmol) of trifluoromethanesulfonic acid was added. The solution was allowed to warm up to 25 °C and stirred for 1 h. An excess of satd. sodium bicarbonate solution (ca. 20 ml) was added, and after 15 min the mixture was extracted with ether (3 × 50 ml). The combined organic layers were washed with water (2 × 20 ml) and dried with magnesium sulfate. After rotary evaporation of the solvent, the yellowish oil was purified by preparative column chromatography on silica gel, using pentane/ether (1 : 1) as eluent, yielding 0.530 g (95%) of **10** as colorless viscous oil. – IR (neat): ν = 3600–3250 cm^{-1}, 3060, 2970, 1680, 1595, 1580, 1445, 1365, 1280, 1210, 1000, 920, 740, 690, 650. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.26 (s, 6H, CH_3), 1.92 (t, *J* = 8 Hz, 2H, CH_2), 2.37 (br. s, 1H, OH), 3.12 (t, *J* = 8 Hz, 2H, CH_2), 7.40–8.00 (m, 5H, aromatic H). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 29.3 (q, CH_3), 33.6 (t, CH_2), 37.2 (t, CH_2), 70.1 (s, C-4), 128.0 (d), 128.4 (d), 132.9 (d), 136.9 (s), 200.9 (s, C=O). – MS (70 eV): *m/z* (%) = 174 (47), 159 (19), 115 (25), 105 (100), 77 (36).

The hydroxy ketone **10** was characterized as its 2,4-dinitrophenylhydrazone derivative (red powder), m.p. 181–183 °C (EtOAc).

$C_{18}H_{20}N_4O_5$ (372.4)	Calcd.	C 58.06	H 5.41	N 15.05
	Found	C 58.12	H 5.56	N 14.86

4-Hydroxy-4-methyl-1-phenyl-1-pentanone (**10**) *by Reduction of* **9** *and* **11** *with Triphenylphosphine*: A solution (50 ml) of **9** or **11** in ether (ca. $5 \cdot 10^{-3}$ M) was cooled to 0 °C, and 4.52 g (17.2 mmol) of triphenylphosphine was added. The reaction mixture was stirred for 1 h. TLC comparison [silica gel, ether/methylene chloride (1 : 1)] with an authentic sample of **10** showed that only this alcohol had been formed.

3-Hydroperoxy-6,6-dimethyl-3-phenyl-1,2-dioxolane (**11**): A flame-dried 100-ml round-bottomed flask, equipped with a magnetic spin bar and dropping funnel, was charged under nitrogen with 1.00 g (5.74 mmol) of **7** in 20 ml of absolute methylene chloride. The solution was cooled to 0 °C and 0.86 g (5.73 mmol) of trifluoromethanesulfonic acid was slowly added at this temp., and the resulting mixture was stirred for 1 h at 25 °C. The solution was again cooled to 0 °C, and 1.60 g of sodium acetate, dissolved in 20 ml of 35% hydrogen peroxide, was added at once under vigorous stirring. After 15 min, 20 ml of satd. ammonium sulfate solution was added, and the mixture was extracted with ether (3 × 50 ml). The combined organic layers were washed with water (2 × 20 ml) and dried with magnetic sulfate. After rotary evaporation of the solvent, the oily residue was covered with petroleum ether (30–50 °C) and stored at –30 °C. After ca. 2 d, colorless prisms separated from the solution, which were collected and washed with 10 ml of cold petroleum ether, dried at 0.1 Torr, yielding 1.10 g (93%) of **11** as colorless prisms, m.p. 57–59 °C. – IR ($CDCl_3$): ν = 3550–3450 cm^{-1}, 3070, 3040, 2980, 1600, 1490, 1450, 1370, 1310, 1235, 1115, 1040, 1020. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.42 (s, 3H, CH_3), 1.55

(s, 3H, CH_3), 1.85 – 1.93, 2.07 – 2.21, 2.38 – 2.45 (each m, 4H, CH_2CH_2), 7.34 – 7.60 (m, 5H, aromatic H), 8.46 (s, 1H, OOH). – ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 28.0 (q, CH_3), 29.5 (q, CH_3), 37.2 (t, CH_2), 37.9 (t, CH_2), 86.1 (s, C-6), 113.8 (s, C-3), 125.7 (d), 128.2 (d), 140.3 (s). – MS (70 eV): *m/z* (%) = 175 (48), 105 (100), 77 (32).

$C_{12}H_{16}O_4$ (224.3) Calcd. C 64.27 H 7.19
Found C 64.08 H 7.23

CAS Registry Numbers

1: 2050-07-9 / **2**: 117861-39-9 / **7**: 1078-36-0 / **8**: 117861-40-2 / **9**: 117861-41-3 / **10**: 117861-42-4 / **10** (2,4-dinitrophenylhydrazone): 117861-44-6 / **11**: 117861-43-5 / O_2: 7782-44-7

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