Thermolysis of 3,3-Bis(phenylmethyl)-1,2-dioxetane: Radical-Induced Formation of the Unusual Decomposition Product 3-Phenyl-1-(phenylmethoxy)-2-propanone

Waldemar Adam* and Simone Andler[1]

Contribution from the Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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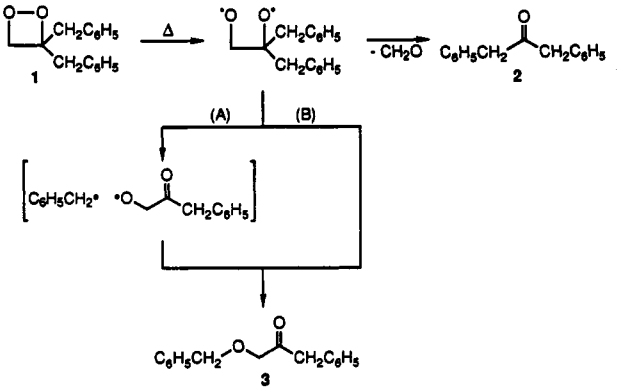
Abstract: The formation of the *rearrangement ketone* 3-phenyl-1-(phenylmethoxy)-2-propanone (**3**) in the thermolysis of 3,3-bis(phenylmethyl)-1,2-dioxetane (**1**) was rigorously probed for radical-induced chain decomposition. The latter mechanism appears to operate on the basis of the following experimental facts: (a) thermolysis of a mixture of the dioxetanes **1**-h_4 and **1**-d_4 afforded significant amounts of the crossover β-keto ethers **3**-h_2 and **3**-d_2, (b) decomposition in toluene-d_8 in the presence of *tert*-butyl peroxalate (**4**) resulted in substantial incorporation of externally generated phenylmethyl-d_7 radicals in the form of the β-keto ether **3**-d_7, and (c) in the presence of the triplet quenchers dibromomethane and 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) the formation of the β-keto ether **3** was suppressed. Clearly, in the thermolysis of dioxetane **1**, free phenylmethyl radicals are generated through Norrish type I cleavage of triplet-excited 1,3-diphenyl-2-propanone (**2**). Attack on the dioxetane peroxide bond leads to the β-keto ether **3** by β cleavage of the resulting alkoxy radical with regeneration of the chain-carrying phenylmethyl radical.

Since their discovery in 1969,[2] much effort has been invested in understanding the mechanism of the thermal decomposition of 1,2-dioxetanes, especially their characteristic properties of generating electronically excited carbonyl products, preferentially triplet states. The *merged mechanism*[3] has been suggested to unify the concerted[4] and the two-step diradical[5] pathways, in order to account most consistently for the large volume of kinetic and product data. In a recent theoretical study is was concluded that the singlet dioxyl diradical is generated without any activation energy;[6] the rate-determining step entails dioxetane C–C bond cleavage on the triplet-excited energy surface.

To date direct experimental evidence for the formation of 1,4-dioxyl diradicals is scarce. On one hand, it was reported that such intermediates could be trapped in the form of its 1,2-diol product when 3,3-dimethyl-1,2-dioxetane was thermally decomposed in 1,4-cyclohexadiene as the hydrogen atom donor.[7] On the other hand, we observed that in the thermolysis of 3,3-bis(phenylmethyl)-1,2-dioxetane (**1**), besides the normal cleavage ketone 1,3-diphenyl-2-propanone (**2**), also the β-keto ether 3-phenyl-1-(phenylmethoxy)-2-propanone (**3**) was obtained in significant amounts (ca. 30–40%).[8] For the formation of the rearrangement ketone **3**, the mechanism in Scheme 1 was

Scheme 1



suggested, in which an O–O bond cleavage leads first to the 1,4-dioxyl diradical. Subsequently, β cleavage generates a pair of phenylmethyl and β-ketoalkoxy radicals, which on in-cage radical coupling affords the β-keto ether **3** (Scheme 1, pathway A). Alternatively, an intramolecular 1,3-alkyl shift produces concertedly the rearrangement ketone **3** (Scheme 1, pathway B).

Radical-induced chain decomposition of dioxetane **1**, initiated by phenylmethyl radicals produced by Norrish type I cleavage of triplet-excited 1,3-diphenyl-2-propanone (**2**) formed in the dioxetane thermolysis, was discarded on the basis of a number of control experiments. Thus, the kinetics of dioxetane **1** decomposition and the product ratio of ketones **2** and **3** were insensitive over a wide range of dioxetane concentrations and radical scavengers (galvinoxyl)[8] also caused no changes.

In an effort to differentiate mechanistically between the diradical pathways A (stepwise) and B (concerted) for the formation of the rearrangement ketone **3** (Scheme 1), we were obliged to scrutinize more rigorously for radical-induced chain decomposition of dioxetane **1**. Our present experimental results, i.e. crossover experiments with the deuterium-labeled dioxetane **1**-d_4, *tert*-butyl peroxalate-induced decompositions in toluene, and triplet quenching experiments with the azoalkane 2,3-

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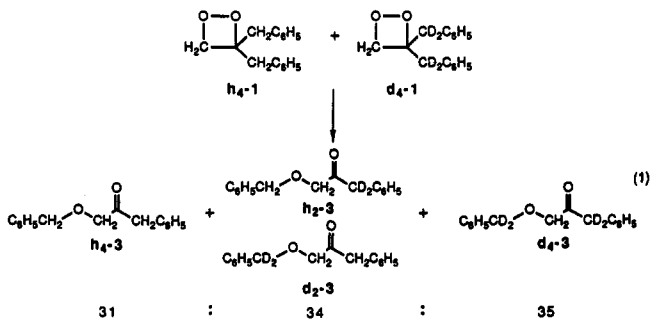
diazabicyclo[2.2.1]hept-2-ene (DBH) and dibromomethane, require a revision of our previous mechanistic conclusions. Thus, the β-keto ether **3** is not directly produced from the 1,4-dioxyl diradical; rather, the major route of its formation entails phenylmethyl radical-induced chain decomposition of dioxetane **1**.

Results

The required deuterated β-bromo hydroperoxide, namely, 1-bromo-2-hydroperoxy-3-phenyl-2-(phenylmethyl-d_2)-propane-*3,3-*d_2, was prepared in 77% yield according to the literature procedure[9] for the undeuterated compound by reaction of 85% H_2O_2 and 1,3-dibromo-5,5-dimethylhydantoin (DDH) with the olefin 3-phenyl-2-(phenylmethyl-d_2)-1-propene-*3,3-*d_2. The latter was prepared in a Takai reaction[10] from 1,3-diphenyl-2-propanone-*1,1,3,3-*d_4[11] (70% yield). NaOH-catalyzed cyclization of the β-bromo hydroperoxide afforded the dioxetane **1**-d_4 (63% yield), conducted according to the literature procedure[9] for the undeuterated compound **1**-h_4. The same degree of deuteration (ca. 97±3%) in the starting material, 1,3-diphenyl-2-propanone-*1,1,3,3-*d_4, was found in the product after the three reaction steps. A thermolyzed, equimolar mixture of dioxetanes **1**-h_4 and **1**-d_4 was submitted to chemical ionization mass spectrometry, which revealed the presence of the undeuterated and the fully deuterated β-keto ethers **3**-h_4 and **3**-d_4 and the crossover β-keto ethers **3**-h_2 and **3**-d_2 in the relative distribution **3**-h_4:**3**-h_2 + **3**-d_2:**3**-d_4 of 31:34:35 (eq 1). To secure that the crossover β-keto ethers **3**-h_2 and



(1)

3-d_2 did not come from the decomposition of the fully deuterated dioxetane **1**-d_4 alone or from a H/D exchange during the mass-spectral analysis, a control experiment was performed in which dioxetanes **1**-h_4 and **1**-d_4 were allowed to decompose separately and the decomposates were thoroughly mixed and submitted to chemical ionization mass spectrometry. About 5% of the possible crossover β-keto ethers **3**-h_2 and **3**-d_2 were observed, of which a substantial portion derives from incomplete deuteration of the starting dioxetane **1**-d_4. The problem with the quantitative mass spectral analysis is the large error due to overlapping m/e peaks; nevertheless, extensive crossover is clearly evident in the thermolysis of a mixture of the **1**-h_4 and **1**-d_4 dioxetanes (eq 1).

Deliberate radical-induced decomposition of the dioxetane **1**-h_4 was probed with di-*tert*-butyl peroxalate (**4**) as radical source. Peroxalate **4** conveniently decays at a reasonably low temperature, e.g. its half-life time ($t_{1/2}$) is 700 min at 25 °C, to generate *tert*-butoxy radicals.[12] Therefore, the thermolysis of dioxetane **1**-h_4 was carried out in the presence of peroxalate **4** by varying the solvent and the concentration of **4** (Table 1, entries 1–5). The ratio of the ketone products **2**-h_4 and **3**-h_4 was determined by ^{1}H NMR spectroscopy (cf. the Experimental Section).

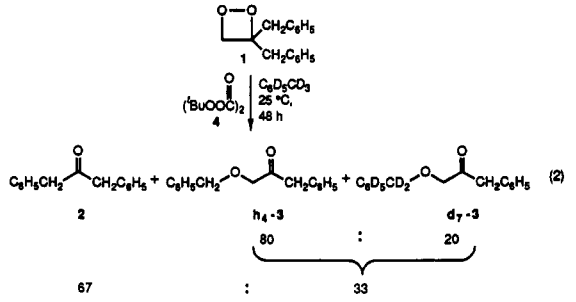
Table 1. Effect of Radical Sources and Triplet Quenchers on the Product Distribution in the Thermal Decomposition of Dioxetane **1**[a]

entry	solvent	[1] × 10² [M]	additive[b]	*t* [h][c]	mb [%][d]	product distribution [%][e] **2**	**3**
1	C_6D_6	4.0		48	95	96	4
2	C_6D_6	4.5	**4** (100)	48	88	99	1
3	$C_6D_5CD_3$	4.5		72	95	94	6
4	$C_6D_5CD_3$	3.1	**4** (7)	72	90	76	24
5	$C_6D_5CD_3$	3.2	**4** (91)	72	88	63	33
6[f]	CH_2Cl_2	10.8		48	90	79	21
7	CH_2Cl_2	13.3	DBH[g] (150)	40	95	96	4
8	CH_2Br_2[h]	2.1		40	95	96	<1

[a] NMR experiments, except entry 8. [b] In parentheses are given the mol % of additive relative to dioxetane **1**. [c] At room temperature (ca. 25 °C). [d] Mass balance. [e] Determined by ^{1}H NMR spectroscopy of the appropriate resonances, normalized to 100%, error ca. 5% of the stated values, 100% consumption of the dioxetane. [f] Reference 8. [g] 2,3-Diazabicyclo[2.2.1]hept-2-ene (DBH) as the triplet quencher (ref 13). [h] CH_2Br_2 as the triplet quencher (ref 14); 4% of the reduction product 3-phenyl-2-(phenylmethyl)-1,2-propanediol was also detected.

In benzene, no significant influence on the product ratio could be observed within the experimental error (±5%), even when a 1:1 mixture of **1**-h_4 to **4** was employed. In the presence or absence of peroxalate **4**, the β-keto ether **3**-h_4 was detected in only small amounts (entries 1 and 2).

A totally different situation was found with toluene-d_8 as the solvent. The ratio of 94:6 for ketones **2**-h_4 and **3**-h_4 in the absence of peroxalate **4** (entry 3) changed to a significantly higher amount of the β-keto ether **3**-h_4 in the presence of **4** (entries 4 and 5), with an appreciable concentration effect on the peroxalate **4**. Thus, the amount of β-keto ether **3**-h_4 increased from 24% for a ca. 15:1 ratio of **1**-h_4 to **4** (entry 4) to 33% for a ca. 1:1 ratio (entry 5). Consequently, the decomposate of dioxetane **1**-h_4 in toluene-d_8 in the presence of peroxalate **4** was examined by quantitative ^{2}H NMR spectroscopy, which showed a broad singlet at δ 4.51 ppm for $C_6D_5CD_2$. The incorporation of toluene-derived phenylmethyl groups in β-keto ether **3**-h_4 was established to be ca. 20% (eq 2). Chemical ionization mass spectrometry confirmed



(2)

the presence of the $C_6D_5CD_2$ group in the β-keto ether **3**-d_7 through the observation of the expected [M + 1] peak at m/e 247.1.

Triplet quenching in the thermal decomposition of dioxetane **1**-h_4 was probed with the efficient triplet quenchers DBH[13] and CH_2Br_2,[14] which are chemically inert to the dioxetane. Indeed, the azoalkane DBH in CH_2Cl_2 as the solvent increased the ketone **2**:**3** ratio from 79:21 (entry 6) to 96:4 (entry 7), as determined by ^{1}H NMR spectroscopy, which indicates almost complete suppression of the β-keto ether **3**-h_4. With CH_2Br_2 as the solvent instead of CH_2Cl_2, triplet quenching was still more effective in that only traces (<1%) of β-keto ether **3**-h_4 could be detected (entry 8).

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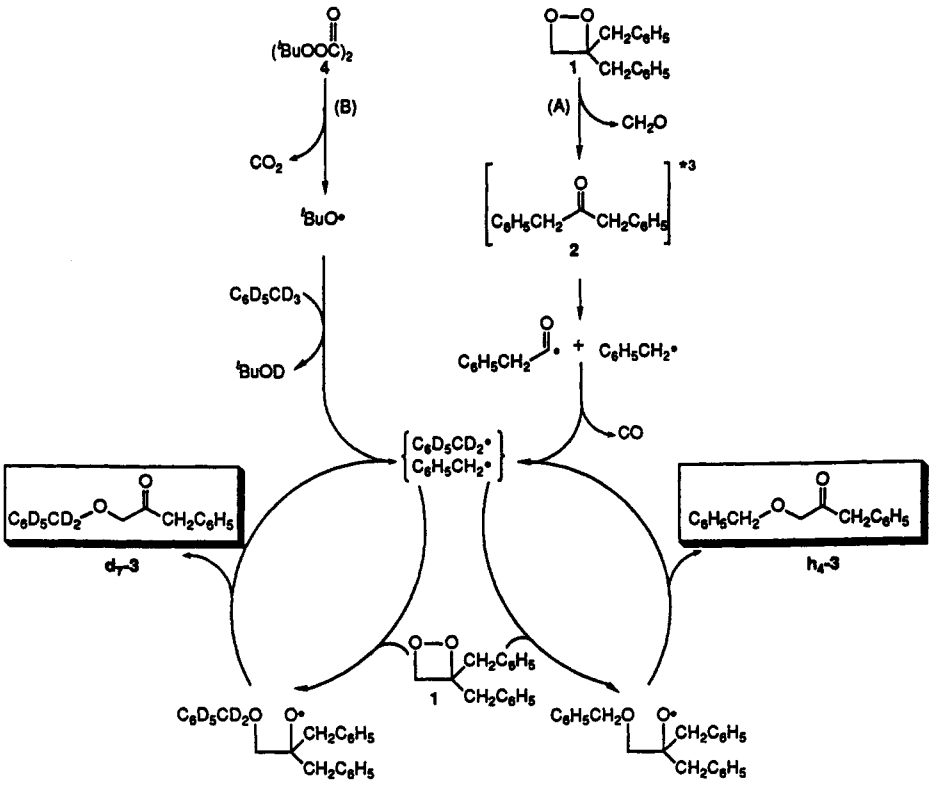
Scheme 2



Mechanistic Discussion

The following three new facts, given above in the Results, established unequivocally induced decomposition by phenylmethyl radicals in the formation of the β-keto ether **3** during the thermal decomposition of the dioxetane **1**: (a) substantial production of the crossover β-keto ethers **3**-h_2 and **3**-d_2 in the neat thermolysis of the mixture of dioxetanes **1**-h_4 and **1**-d_4 (eq 1), as established by mass spectrometry, (b) significant incorporation of externally generated phenylmethyl-d_7 radicals in the form of the β-keto ether **3**-d_7 during the thermolysis of dioxetane **1**-h_4 in toluene-d_8 through the action of di-*tert*-butyl peroxalate (**4**) as radical source (eq 2), and (c) suppression of the β-keto ether **3** product during the thermolysis of the dioxetane **1** in the presence of the triplet quenchers DBH and dibromomethane (Table 1, entries 7 and 8).

We offer the mechanism in Scheme 2 to rationalize these results, in which we address only the formation of the unusual *rearrangement product*, namely the β-keto ether **3**. The generation of the normally expected fragmentation ketone, in this case 1,3-diphenyl-2-propanone (**2**), which figures as the major product, arises from the usual retrocleavage of the dioxetane ring and is not explicitly included in Scheme 2, except that in its triplet-excited state it generates phenylmethyl radicals by Norrish type I fragmentation.

The right-hand branch (Scheme 2, pathway A) portrays the decomposition mode under normal conditions, especially in the neat phase, while the left-hand branch (Scheme 2, pathway B) displays the sequence of events under the action of peroxalate **4** in toluene. Thus, along pathway A, the usual dioxetane thermolysis generates preferentially triplet ketone **2** by fragmentation, which suffers Norrish type I cleavage to afford phenylmethyl radicals.[5c,15] Subsequent attack by $PhCH_2^\bullet$ at the sterically more exposed oxygen atom of the dioxetane peroxide bond affords an alkoxy radical. The latter regenerates phenylmethyl radicals and the β-keto ether **3**-h_4 by β scission. Such cleavage is particularly facile for phenylmethyl radicals and is well established.[16]

When a 1:1 mixture of the dioxetanes **1**-h_4 and **1**-d_4 is decomposed in the neat phase, independently $PhCH_2^\bullet$ and $PhCD_2^\bullet$ radicals are produced by pathway A. Their attack on the two dioxetanes **1**-h_4 and **1**-d_4 should afford the crossover β-keto ethers **3**-h_2 and **3**-d_2. Although the statistical distribution of all possible β-keto ethers is not achieved (eq 1), clearly substantial crossover (fact a) has been observed, in support of the proposed phenylmethyl radical-induced decomposition in Scheme 2.

Alternatively, triplet quenchers should suppress phenylmethyl radical production by deactivation of the triplet ketone **2** and thus prevent the Norrish type I cleavage. Indeed, both triplet quenchers DBH and CH_2Br_2 efficiently reduce the formation of the β-keto ether **3** product (fact c). Clearly, when the formation of phenylmethyl radicals is prevented, the induced decomposition of the dioxetane **1** no longer operates and the normal fragmentation to afford ketone **2** prevails. The advantage of CH_2Br_2 and DBH as triplet quenchers is that they do not chemically react with the dioxetane **1**.[8]

The most convincing evidence in support of the mechanism in Scheme 2 is the incorporation of externally generated phenylmethyl radicals (fact b), when the dioxetane **1**-h_4 is decomposed in the presence of peroxalate **4** as the radical source (eq 2). This can only be discerned when perdeuterated toluene ($C_6D_5CD_3$) is employed as the solvent, since then the $C_6D_5CD_2^\bullet$ radicals derived from the solvent can readily be distinguished from the $C_6H_5CH_2^\bullet$ radicals generated by the dioxetane **1**-h_4.

As pathway B in Scheme 2 exhibits, thermal decomposition of the peroxalate **4** constitutes an effective source of *t*-BuO$^\bullet$ radicals at room temperature,[12] which abstract deuterium atoms from toluene-d_8 to afford $C_6D_5CD_2^\bullet$ radicals. These then enter into the radical-induced decomposition cycle by reacting with the dioxetane **1**-h_4 to produce the oxyl radical, which in turn undergoes β scission to give the β-keto ether **3**-d_7 and $C_6H_5CH_2^\bullet$ radicals. The latter lead to the β-keto ether **3**-h_4, as already

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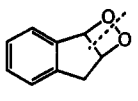
discussed in the pathway A process. Since the β-keto ether **3**-h_4 product dominates 4-fold over **3**-d_7, externally generated radicals are incorporated significantly less efficiently than those derived from the dioxetane. Presumably the steady-state concentration of phenylmethyl radicals generated in the peroxalate decomposition is appreciably lower than that produced in the dioxetane decomposition. For example, when the concentration of peroxalate **4** is increased 10-fold, the yield of **3**-h_4 and **3**-d_7 β-keto ethers is raised by only ca. 30% (Table 1, entries 4 and 5). Nevertheless, this moderate increase is significant and substantiates the radical-induced mechanism of Scheme 2. This result also implies that the chain length of the phenylmethyl radical-induced decomposition is quite short. If it were long, essentially exclusive formation of β-keto ether **3**-d_7 would have been expected.

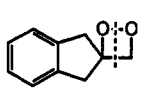
In benzene-d_6, from which deuterium abstraction by *t*-BuO• is difficult, no difference in the product composition with or without peroxalate **4** was found. Possibly, also benzene quenches the Norrish type I cleavage of the triplet-excited 1,3-diphenyl-2-propanone (**2**) and, therefore, no radical-induced decomposition of the dioxetane **1** takes place.

The present results establish unquestionably that free phenylmethyl radicals intervene in the thermal decomposition of dioxetane **1**. They are responsible for the formation of the unusual *rearrangement product*, namely the β-keto ether **3**, through radical-induced decomposition (Scheme 2). Thus, dioxetane **1** is the first case in which a product of radical-induced decomposition could be observed.

Nevertheless, dioxetane **1** has been quite elusive in revealing its propensity for radical-induced decomposition and has evaded the usual mechanistic probes for such processes, as manifested by the lack of dioxetane concentration effects on the kinetics and product distribution and the inability to intervene with radical scavengers. Consequently, our present results (experimental facts a–c) oblige us to conclude that the β-keto ether **3** does not constitute *bona fide* evidence for 1,4-dioxyl diradicals in the thermal decomposition of dioxetane **1**. This does not necessarily imply that such diradicals do not intervene, but if they are genuine intermediates, their expulsion of phenylmethyl radicals (Scheme 1) is of minor importance compared to dioxetane C–C bond homolysis to the excited carbonyl fragments, predominantly the triplet ketone **2**. On β scission, the latter serves as source for $PhCH_2$• radicals, which are responsible for the formation of β-keto ether **3** through radical-induced decomposition of the dioxetane **1** (Scheme 2). All claims to propose sufficiently persistent 1,4-dioxyl diradicals as direct precursors[7] for unusual decomposition products derived from dioxetanes should, therefore, be carefully scrutinized.

In view of our present results (Scheme 2), it is not surprising that we have been unable to find additional dioxetanes which generate β-keto ether products as observed for the bis(phenylmethyl)-substituted derivative **1**. For example, the thermal decomposition of the related dioxetanes below gave exclusively the expected cleavage products along the dashed lines.[1] Of course,





free phenylmethyl-type radicals cannot be generated in these cases and the induced decomposition mechanism does not operate. Thus, the dioxetane **1** constitutes a special and optimal case for such a radical-induced process, despite the fact that it has been cumbersome to unravel it.

To summarize, the substantial formation of the crossover products **3**-h_2 and **3**-d_2 in the decomposition of a mixture of the dioxetanes **1**-h_4 and **1**-d_4, the suppression of the formation of the β-keto ether **3** on addition of the triplet quenchers CH_2Br_2 and DBH, and the significant incorporation of independently generated phenylmethyl-d_7 radicals in the β-keto ether **3** during the thermolysis of dioxetane **1**-h_4 in the presence of *tert*-butyl peroxalate (**4**) in toluene-d_8 speak against our former mechanistic proposal,[8] i.e. β cleavage of the intermediary 1,4-dioxyl diradical (Scheme 1). Instead, the radical-induced chain mechanism in Scheme 2 appears to operate, in which thermal decomposition of the dioxetane **1** generates the necessary phenylmethyl radicals through Norrish type I cleavage of triplet-excited 1,3-diphenyl-2-propanone (**2**). In principle, this radical chain process is akin to the quantum chain process for the triplet acetone-sensitized decomposition of tetramethyl-1,2-dioxetane,[17] although the latter does not reveal itself in the products formed.

Experimental Section

General Aspects. Melting points were determined on a Reichert Thermovar Kofler apparatus. The IR spectra were recorded on a Perkin-Elmer 1420 instrument. ^1H NMR spectra were run on a Bruker AC 200 (200 MHz) or a Bruker AC 250 (250 MHz) with TMS as the internal standard. The degree of deuteration was determined by ^1H NMR spectroscopy (ratio of aromatic to benzylic protons). ^2H NMR spectra were obtained on a Bruker WM 400 (61.4 MHz) spectrometer with acetone-d_6 as the internal standard. ^{13}C NMR spectra were determined on a Bruker AC 200 (50 MHz) or on a Bruker AC 250 (63 MHz) with chloroform-*d* as the internal standard. The mass spectra were obtained on a Varian MATCH 8200. Elemental analysis was performed by the Analytical Division of the Institute of Inorganic Chemistry (University of Würzburg). Thin layer chromatography (TLC) was performed on a Polygram SIL G/UV_{254} (40 × 80) from Machery & Nagel Co. Peroxides were detected with 10% aqueous KI/HOAc solution, other compounds by irradiation with an UV lamp (254 nm). Column chromatography was performed on silica gel (63–200 μm) from Woelm as the stationary phase with an adsorbant/substrate ratio of 100:1. The required 1,3-diphenyl-2-propanone-*1,1,3,3*-d_4,[10] dioxetane **1**-h_4,[9] and di-*tert*-butyl peroxalate (**4**)[12] were prepared according to literature procedures.

Caution! *3,3-Disubstituted 1,2-dioxetanes tend to decompose spontaneously and violently at room temperature. All safety precautions must be strictly observed!*

3-Phenyl-2-(phenylmethyl-d_2)-1-propene-*3,3*-d_2. Under an argon gas atmosphere, 10.7 g (40.0 mmol) of diiodomethane was added at 25 °C to a stirred suspension of 4.70 g (72.0 mmol) of zinc in 60 mL of THF. After 30 min, a solution of 1.52 g (8.00 mmol) of $TiCl_4$ in 8 mL of CH_2Cl_2 was added at 0 °C and a dark brown solution resulted, which was stirred for another 30 min at 25 °C. Within 30 min, 1.71 g (8.00 mmol) of 1,3-diphenyl-2-propanone-*1,1,3,3*-d_4 was added and the solution stirred for about 25 min. After washing with 100 mL of HCl and 50 mL of a saturated, aqueous solution of NaCl and drying over $MgSO_4$, the solvent was evaporated (25 °C, 15 Torr). Silica gel chromatography [100:1 petroleum ether (bp 30–50 °C)/diethyl ether as the eluent] of the brown residue afforded 1.19 g (70%) of a colorless oil (the degree of deuteration was 97±3%, as established by ^1H NMR spectroscopy): TLC [100:1 petroleum ether (30–50)/diethyl ether] R_f = 0.22; ^1H NMR ($CDCl_3$, 250 MHz) δ 4.90 (s, 2H, $=CH_2$), 7.18–7.38 (m, 10H, arom. H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ 41.7 (quin, J = 15.7 Hz, CD_2Ph), 113.3 (t, $=CH_2$), 126.1 (d), 128.3 (d), 129.0 (d), 139.4 (s), 148.2 (s, $C=CH_2$).

1-Bromo-2-hydroperoxy-3-phenyl-2-(phenylmethyl-d_2)-propane-*3,3*-d_2. The β-bromo hydroperoxide was prepared according to the procedure for the undeuterated compound[9] by reaction of 3-phenyl-2-(phenylmethyl-d_2)-1-propene-*3,3*-d_2 with 1,3-dibromo-5,5-dimethylhydantoin and H_2O_2 (85% aqueous solution). This product was obtained as colorless needles, mp 94.5–95.5 °C (77% yield) (the degree of deuteration was 97±3%, as established by ^1H NMR spectroscopy): TLC (CH_2Cl_2) R_f = 0.56; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.35 (s, 2H, CH_2Br), 7.30–7.40 (m, 10H, arom. H), 7.76 (s, 1H, OOH); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 35.2 (t, CH_2Br), 37.7 (quin, J = 19.4 Hz, CD_2Ph), 85.4 (s, $C(CD_2Ph)_2$), 126.7 (d), 128.2 (d), 130.5 (d), 135.4 (s); IR (CCl_4) 3520–3500 (OOH), 3060, 3040, 3000, 1585, 1480, 1430, 1415, 1315, 1245, 1225 cm^{-1}. Anal. Calcd for $C_{16}H_{13}BrO_2$: C, 59.10; H, 6.51. Found: C, 59.37; H, 6.67.

3,3-Bis(phenylmethyl-d_2)-1,2-dioxetane (1-d_4). The dioxetane **1**-d_4 was prepared according to the literature procedure for the undeuterated dioxetane **1**-h_4[9] by NaOH-catalyzed cyclization of 1-bromo-2-hydroperoxy-3-phenyl-2-(phenylmethyl-d_2)-propane-*3,3*-d_2 to afford yellow needles, mp 58–59 °C (63% yield) (the degree of deuteration was 97±3%, as established by ^1H NMR spectroscopy): TLC (CH_2Cl_2) R_f = 0.66; ^1H

(17) Lechtken, P.; Yekta, A.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3027–3028.

NMR ($CDCl_3$, −20 °C, 200 MHz) δ 5.04 (s, 2H, CH_2O), 7.20–7.40 (m, 10H, arom. H); ^{13}C NMR ($CDCl_3$, −20 °C, 50 MHz) δ 42.3 (quin, J = 19.6 Hz), CD_2Ph), 77.8 (t, CH_2O), 88.4 (s, $C(CD_2Ph)_2$), 127.0 (d), 128.4 (d), 130.1 (d), 135.0 (s).

Crossover Products in the Decomposition of a Mixture of Dioxetanes 1-h_4 and 1-d_4. A solution of 17.5 mg (72.8 μmol) of 1-h_4 and 17.8 mg (72.8 μmol) of 1-d_4 was prepared in 0.5 mL of CH_2Cl_2. The solvent was removed by evaporation at 0 °C and 20 Torr, and the mixture of dioxetanes was stored at room temperature (ca. 25 °C) under an argon gas atmosphere in the dark. After 48 h, the decomposition of the dioxetanes was complete (negative KI/HOAc test), resulting in a yellow oil (mass balance > 95%). The relative product distribution (normalized to 100%) of 3-h_4:3-h_2 + 3-d_2:3-d_4 was determined by chemical ionization mass spectroscopy to be 31:34:35 (error ±10% of stated values).

Test for Crossover Products in the Mass-Spectral Analysis of Separately Decomposed Dioxetanes 1-h_4 and 1-d_4. Samples of 15.1 mg (0.063 mmol) of 1-h_4 and 15.5 mg (0.063 mmol) of 1-d_4 were decomposed separately at 25 °C for 48 h (negative KI/HOAc test). The resulting yellow oils (mass balance >95%) were mixed and examined by chemical ionization mass spectroscopy. The relative amount of the crossover β-keto ethers 3-h_2 and 3-d_2 was determined to be ca. 5%.

Decomposition of Dioxetane 1-h_4 in Various Solvents. Aliquots (0.5–0.6 mL) of 0.03–0.05 M dioxetane 1-h_4 solutions (solvents are given in Table 1) were kept at room temperature (ca. 25 °C) under an argon gas atmosphere until complete decomposition (negative KI/HOAc test, reaction times are given in Table 1). The relative product distributions were determined by ^1H NMR spectroscopy with hexamethyldisiloxane as the internal standard. The results are given in Table 1.

Decomposition of Dioxetane 1-h_4 in the Presence of Di-*tert*-butyl Peroxalate (4). Aliquots (0.6 mL) of 0.03–0.05 M dioxetane 1-h_4 solutions (solvents are given in Table 1), which contained peroxalate **4** (amounts in mol % relative to the dioxetane 1-h_4 are given in Table 1) and hexamethyldisiloxane as the internal NMR standards were kept at room temperature (ca. 25 °C) until complete decomposition of the dioxetane 1-h_4 (^1H NMR monitoring). The relative product distributions were determined by ^1H NMR spectroscopy, and the results are given in Table 1.

Evidence for the Incorporation of Deuterated Phenylmethyl Radicals in Keto Ether 3 by ^2H NMR Spectroscopy and Mass Spectrometry. Samples of 52.8 mg (0.220 mmol) of dioxetane 1-h_4 and 50.8 mg (0.217 mmol, 99 mol %) of peroxalate **4** were dissolved in 1.50 mL of toluene-d_8 and kept at 25 °C for 48 h in the dark. The solvent was evaporated (25 °C and 0.1 Torr) to afford 79.5 mg (94%) of a yellow oil, which was taken up in $CFCl_3$. Quantitative ^2H NMR spectroscopy established 20±7% incorporation of deuterated phenylmethyl radicals in keto ether **3**. Mass spectroscopy showed the expected [M + 1] peak at m/e 247.3 [M + 1] (20% relative intensity) for the β-keto ether 3-d_7.

3-Phenyl-1-(phenyl-d_5-methoxy-d_2)-2-propanone (3-d_7): ^2H NMR ($CFCl_3$, 61.4 MHz) δ 4.51 (br. s, 2D, $CD_2C_6D_5$), 7.20–7.40 (m, 5D, $CD_2C_6D_5$).

Decomposition of Dioxetane 1-h_4 in the Presence of CH_2Br_2 as the Triplet Quencher. A sample of 9.80 mg (41.0 μmol) of dioxetane 1-h_4 was dissolved in 10.4 mg (60.0 μmol) of CH_2Br_2, and the solution was stored at 25 °C in the dark for 40 h until complete decomposition of the dioxetane (negative KI/HOAc test). Evaporation of the solvent afforded 9.20 mg (94%) of a yellow oil which contained a mixture of 2-h_4, 3-h_4, and the reduction product 3-phenyl-2-(phenylmethyl)-1,2-propanediol in a ratio of 96:<1:4, as determined by ^1H NMR spectroscopy (Table 1).

Decomposition of Dioxetane 1-h_4 in the Presence of Diazabicyclo-[2.2.1]hept-2-ene (DBH) as the Triplet Quencher. A solution of 9.50 mg (40.0 μmol) of dioxetane 1-h_4 and 5.65 mg (60.0 μmol) of DBH in 0.3 mL of CH_2Cl_2 was kept at room temperature (ca. 25 °C) for 40 h until complete consumption of the dioxetane (negative KI/HOAc test). Evaporation of the solvent yielded 9.10 mg (95%) of a yellow oil. The relative product distribution was determined by ^1H NMR spectroscopy, and the results are given in Table 1.

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