Novel photo-rearrangements of 3,3,5-triaryl-1,2-dioxolanes: evidence for 1,5-dioxyl diradical intermediates

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3-(*p*-Methoxyphenyl)-substituted 1,2-dioxolanes undergo novel photo-rearrangements to afford 1,3-diaryl-3-(*p*-methoxyphenoxy)propan-1-ones along with 1,3,3-triaryl-3-hydroxypropan-1-ones *via* 1,5-dioxyl diradical intermediates.

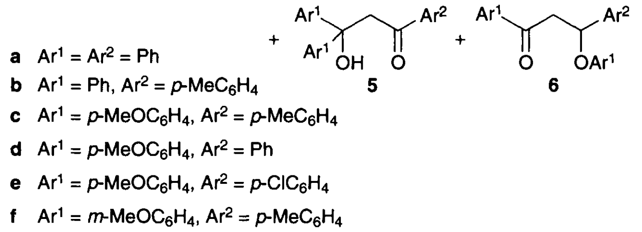
Much attention has been focused on cyclic peroxides from both synthetic and mechanistic viewpoints.[1] In particular, the fragmentation mechanisms for 1,2-dioxolanes and 1,2-dioxanes have been intensively studied in connection with the reactivities of dioxyl diradical species.[2,3] Adam and coworkers proposed that the intermediates are not 1,5-dioxyl diradicals, but are instead 1-oxatrimethylene diradicals in both the photo and thermal reactions of 1,2-dioxolanes [eqn. (1)],[2a] whereas 1,6-dioxyl diradicals are intermediates in the reactions of 1,2-dioxanes [eqn. (2)].[3a] These contrasting results prompted us to re-examine the involvement of 1,5-dioxyl diradicals in the photoreactions of 1,2-dioxolanes. Chemical capture is a useful method for confirming the existence of reactive intermediates, particularly when such species are short-lived, like 1,5-dioxyl diradicals. We designed 3,3,5-triaryl-1,2-dioxolanes **1** as substrates for the photoreactions since the 1,5-dioxyl diradicals, if generated, could be intramolecularly captured by 1,4-hydrogen atom transfer. Herein, we report our results on the photo-rearrangements of **1**, providing clear evidence for the intervention of the 1,5-dioxyl diradicals.

3,3,5-Triaryl-1,2-dioxolanes **1** were prepared by the oxygenation of 1,1,2-triarylcyclopropanes sensitised by triphenylpyrylium perchlorate. Upon irradiation of a nitrogen-purged MeCN (25 ml) solution of 3,3,5-triphenyl-1,2-dioxolane **1a** (0.5 mmol) in a Pyrex tube for 5 h with a 2 kW xenon lamp, benzophenone **2a** (24%), acetophenone **3a** (20%) and benzaldehyde **4a** (13%) were obtained together with the rearranged product, 1,3,3-triphenyl-3-hydroxypropan-1-one **5a** (21%, entry 1 in Table 1, Scheme 1).† Similarly, photoreaction of **1b** produced aldol **5b** (19%) together with fragmentation products **2b**–**4b** (entry 2). Unexpectedly, 1-(*p*-methoxyphenyl)-3-(*p*-methylphenyl)-3-(*p*-methoxyphenoxy)propan-1-one **6c** (19%) was obtained along with aldol **5c** (25%) and other fragmentation products **2c**–**4c** (entry 3) when 3,3-bis(*p*-methoxyphenyl)-5-(*p*-methylphenyl)-1,2-dioxolane **1c** was photolysed under similar conditions. To determine the generality of such aryl transfer, photoreactions of other 3,3-bis(*p*-methoxylphenyl)substituted 1,2-dioxanes **1d** and **1e** were examined. Similar to the case of **1c**, keto ethers **6d** and **6e** were isolated in 23 and 27% yields, respectively (entry 4 and 5). Interestingly, in constrast to the photoreactions of **1c**–**1e**, keto ether **6f** was not obtained at all in the photoreaction of *m*-methoxyphenyl-substituted dioxolane **1f** (entry 6). In order to obtain information about the excited states of **1**, a triplet quenching experiment for **1c** was conducted using 2,5-dimethylhexa-1,3-diene (E_T = 58.7 kcal mol^{-1}; 1 cal = 4.184 J). The formation of **5c** and **6c** was almost completely suppressed, while formation of **2c**–**4c** was not (entry 7). In addition, triplet photo-sensitisation of **1c** using benzophe-

Table 1 Photoreactions of 3,3,5-triaryl-1,2-dioxolanes **1**[a]

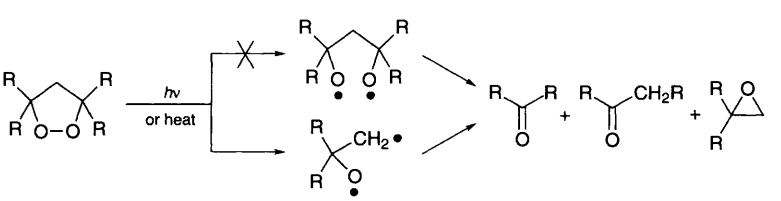
Entry	Dioxolane	Conversion (%)	Yield (%)[b]				
			2	**3**	**4**	**5**	**6**
1	**1a**	86	24	20	13	21	0
2	**1b**	81	13	6	4	19	0
3	**1c**	90	21	6	12	25	19
4	**1d**	93	29	16	8	26	23
5	**1e**	85	20	7	13	14	27
6	**1f**	80	19	7	13	27	0
7[c]	**1c**	47	20	5	22	[d]	[d]
8[e,f]	**1c**	52	22	6	5	14	9
9[f]	**1c**	27	12	3	7	5	3

[a] 2 kW Xe lamp; Pyrex cut; 15–20 °C; **1**, 0.5 mmol; MeCN, 25 ml. [b] Isolated yields by silica gel TLC. [c] 2,5-Dimethylhexa-1,3-diene, 5.0 mmol. [d] Less than 2% yield. [e] Ph_2CO, 0.5 mmol. [f] λ > 340 nm; irradiation time, 5 h.

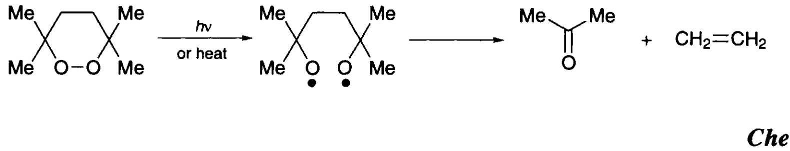


a $Ar^1 = Ar^2 = Ph$
b $Ar^1 = Ph$, $Ar^2 = p\text{-}MeC_6H_4$
c $Ar^1 = p\text{-}MeOC_6H_4$, $Ar^2 = p\text{-}MeC_6H_4$
d $Ar^1 = p\text{-}MeOC_6H_4$, $Ar^2 = Ph$
e $Ar^1 = p\text{-}MeOC_6H_4$, $Ar^2 = p\text{-}ClC_6H_4$
f $Ar^1 = m\text{-}MeOC_6H_4$, $Ar^2 = p\text{-}MeC_6H_4$

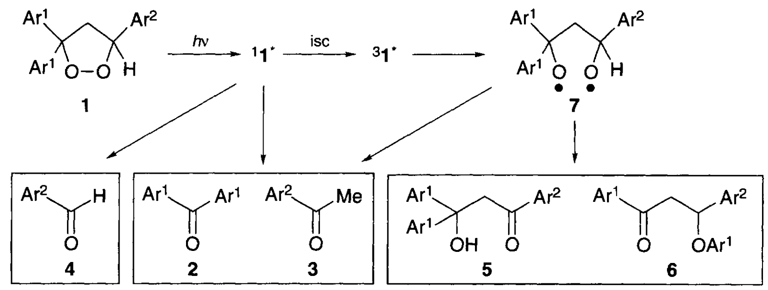
Scheme 1 *Reagents and conditions*: i, *h*ν, N_2, MeCN, 3h



(1)



(2)



Scheme 2

'none enhanced all the product yields except that of **4c** (compare entry 8 with entry 9). In contrast, 4,4′-dimethoxybenzophenone **2c** (99%) and *p*-methylacetophenone **3c** (91%) were isolated exclusively when **1c** was heated at 150 °C for 1.5 h under nitrogen atmosphere.

On the basis of the above results, a plausible mechanism is proposed, as shown in Scheme 2. The formation of **5** and **6** would suggest the intervention of the 1,5-dioxyl diradical **7**. In the photoreactions of **1c–1e**, the excited triplet state of **1** generates the 1,5-dioxyl diradical **7**, which undergoes 1,4-aryl transfer in competition with 1,4-hydrogen transfer to produce rearranged products **5** and **6**, respectively, whereas the fragmentation products **2–4** are produced mainly from the excited singlet state of **1**. In the case of **1a–1b** and **1f**, the generated 1,5-dioxyl diradical **7** predominantly undergoes 1,4-hydrogen transfer to produce **5**. The 1,4-aryl transfer in **7** could be promoted by the attack of electrophilic oxyl radical on the electron-donating *p*-methoxyphenyl group at its ipso carbon. The isolation of **6c–6e** and the lack of **6f** could support this assumption.

We are grateful to Professor Tsutomu Miyashi (Faculty of Science, Tohoku University) and Professor Eietsu Hasegawa (Faculty of Science, Niigata University) for their helpful comments.

Footnotes

† 1,1-Diphenylethylene oxide and 1,2-diphenylethanone were also obtained in the photoreaction of **1a**. All products were isolated by silica gel thin layer chromatography (TLC) and characterised by their spectroscopic data.

Selected data for **5c**: mp 143–143.5 °C; IR (KBr) 3435 (OH), 1660 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 2.41 (3 H, s), 3.75 (6 H, s), 3.83 (2 H, s), 5.49 (1 H, s), 6.64–6.88 (4 H, m), 7.08–7.38 (6 H, m), 7.64–7.90 (2 H, m). For **6c**: oil, IR (neat) 1680 cm^{-1}; ^{1}H NMR (90 MHz, CDCl$_3$) δ 2.28 (3 H, s), 3.13 (1 H, dd, *J* 16.4, 4.4 Hz), 3.64 (3 H, s), 3.75 (1 H, dd, *J* 16.4, 8.2 Hz), 3.79 (3 H, s), 5.74 (1 H, dd, *J* 8.2, 4.4 Hz), 6.58–6.78 (4 H, m), 6.79–7.02 (2 H, m), 7.04–7.20 (2 H, m), 7.24–7.40 (2 H, m), 7.80–8.08 (2 H, m); ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 21.08 (q), 46.97 (t), 55.37 (q), 55.54 (q), 77.53 (d), 113.72 (d), 114.48 (d), 117.62 (d), 126.19 (d), 129.33 (d), 130.30 (s), 130.58 (d), 137.40 (s), 138.65 (s), 152.14 (s), 154.14 (s), 163.63 (s), 195.64 (s).

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Received, 30th July 1996; Com. 6/05324F