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.
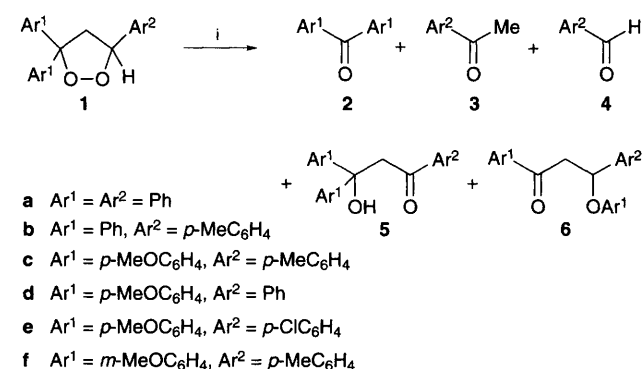
3,3,5-Triaryl-1,2-dioxolanes 1 were prepared by the oxygenation of 1,1,2-triarylcyclopropanes sensitised by triphenylpyrylium perchlorate. Upon irradiation of a nitrogen-purged MeCN (25 ml) solution of 3,3,5-triphenyl-1,2-dioxolane 1a (0.5 mmol) in a Pyrex tube for 5 h with a 2 kW xenon lamp, benzophenone 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 contrast 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-

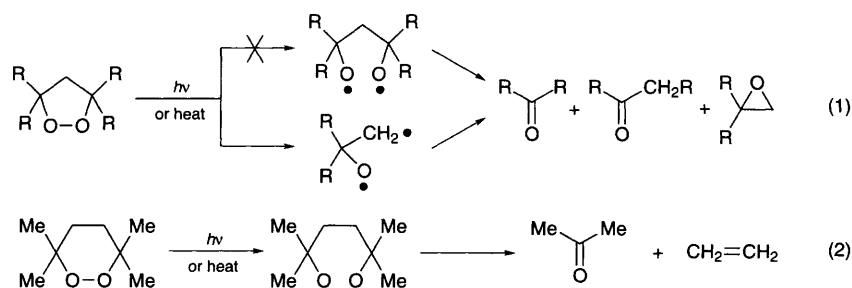**Table 1** Photoreactions of 3,3,5-triaryl-1,2-dioxolanes 1[a]

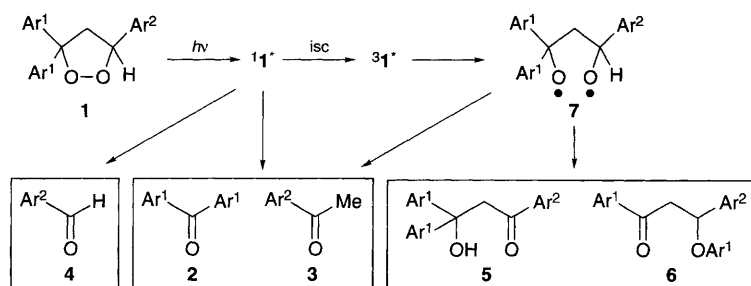| Entry	Dioxolane	Conversion (%)	Yield (%)[b]				
			2	3	4	5	6
1	1a	86	24	20	13	21	0
2	1b	81	13	6	4	19	0
3	1c	90	21	6	12	25	19
4	1d	93	29	16	8	26	23
5	1e	85	20	7	13	14	27
6	1f	80	19	7	13	27	0
7[c]	1c	47	20	5	22	[d]	[d]
8[e,f]	1c	52	22	6	5	14	9
9[f]	1c	27	12	3	7	5	3

[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$_2$CO, 0.5 mmol. [f] λ > 340 nm; irradiation time, 5 h.

a   Ar^1 = Ar^2 = Ph
b   Ar^1 = Ph, Ar^2 = p-MeC$_6$H$_4$
c   Ar^1 = p-MeOC$_6$H$_4$, Ar^2 = p-MeC$_6$H$_4$
d   Ar^1 = p-MeOC$_6$H$_4$, Ar^2 = Ph
e   Ar^1 = p-MeOC$_6$H$_4$, Ar^2 = p-ClC$_6$H$_4$
f   Ar^1 = m-MeOC$_6$H$_4$, Ar^2 = p-MeC$_6$H$_4$

Scheme 1 *Reagents and conditions*: i, hv, N$_2$, MeCN, 3h

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.

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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; ¹H NMR (90 MHz, CDCl₃) 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; ¹H NMR (90 MHz, CDCl₃) 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); ¹³C NMR (22.5 MHz, CDCl₃) 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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