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Tetrahedron Letters 45 (2004) 7423–7428
Tetrahedron Letters

Triphenylpyrylium salt-sensitized photoreactions of 1,4-diaryl-2,3-dioxabicyclo[2.2.2]octanes through competitive single electron-transfer pathway and proton-catalyzed pathway

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Received 3 June 2004; revised 12 August 2004; accepted 13 August 2004

Abstract—2,4,6-Triphenylpyrylium tetrafluoroborate ($TPPBF_4$)-sensitized photoinduced electron-transfer (PET) reactions of 1,4-diaryl-2,3-dioxabicyclo[2.2.2]octanes **5** (**a**: $Ar^1 = Ar^2 = p\text{-}MeOC_6H_4$, **b**: $Ar^1 = Ar^2 = p\text{-}MeC_6H_4$, **c**: $Ar^1 = Ar^2 = Ph$) underwent novel fragmentation through their radical cations to give 1,4-diarylbutan-1,4-diones **6** accompanied by elimination of ethylene. On the other hand, 4-aryl-cyclohex-3-en-1-ones **7**, *p*-substituted phenols **8**, and 4-aryl-4-aryloxycyclohexanones **9** were produced through proton-catalyzed pathways when the PET reactions of **5** were performed in the absence of a certain base such as 2,6-di-*tert*-butylpyridine (DTBP). Particularly, the formation of **9** is consistent with the novel cationic rearrangement involving nucleophilic *O*-1,2-aryl shifts and *C*-1,4-aryl shifts.

Much attention has been devoted to studies on photoinduced electron-transfer (PET) and nonphotochemical single electron-transfer (SET) reactions of organic molecules.[1] In particular, the electrolytic[2] and Fe(II)-induced[3] *reduction* of cyclic peroxides,[4] which results in the cleavage of the weak O–O bond, has been extensively investigated since SET processes of cyclic peroxides are responsible for their chemical[2–4] and antimalarial activities. [3] In contrast, only a few examples on the chemical reactions of cyclic peroxides through the SET *oxidation* have been reported although the cyclic voltammetric behavior of some cyclic peroxides and their radical cations has been intensively investigated.[5] For example, SET *oxidation* of anthracene endoperoxides **1** and 1,4-diphenyl-2,3-dioxabicyclo[2.2.2]oct-5-ene **3**, induced by the photoexcitation of their charge-transfer complexes with tetracyanoethylene[6], underwent C–O bond cleavage to afford **2** and **4**, respectively, along with molecular oxygen ($^1O_2$ and/or $^3O_2$) (Scheme 1).[6a,b]

These results and our interest in this field prompted us to investigate the reactivity of the radial cation species generated through PET processes of saturated-type antimalarial bicyclic peroxides such as 1,4-diaryl-2,3-dioxabicyclo[2.2.2]octanes **5a**–**c**[7] since little work has been done on the PET and SET *oxidation* reactions of **5a**–**c**. For this purpose, we selected 2,4,6-triphenylpyrylium tetrafluoroborate ($TPPBF_4$)[8] as a PET sensitizer since the singlet excited state of $TPPBF_4$ has sufficient electron-accepting ability to generate the radical cations of **5a**–**c**. As described below, we have found that **5a**–**c** underwent a novel transformation through their radical cation intermediates to give 1,4-diarylbutan-1,4-diones **6** and ethylene, whereas **5** concurrently underwent novel proton-catalyzed rearrangement and fragmentation to afford 4-aryl-cyclohex-3-en-1-ones **7**, *p*-substituted phenols **8**, 4-aryl-4-aryloxycyclohexan-1-ones **9**. In addition, we have also found that evidence for the nucleophilic *O*-1,2-aryl shifts and the novel nucleophilic *C*-1,4-aryl shifts was obtained by the isolation of rearrangement products **9**.

When a nitrogen-purged CH_2Cl_2 solution of **5a** (2.0×10^{-2} M), a catalytic amount of 2,4,6-triphenylpyrylium tetrafluoroborate ($TPPBF_4$, 1.0×10^{-3} M), and 2,6-di-*tert*-butylpyridine (DTBP, 1.0×10^{-3} M) as

Keywords: Triphenylpyrylium tetrafluoroborate; 1,4-Diaryl-2,3-dioxabicyclo[2.2.2]octane; Photoinduced electron-transfer; Single electron-transfer; Radical cation; Proton-catalyzed reaction; *O*-1,2-Aryl shift; *C*-1,4-Aryl shift.
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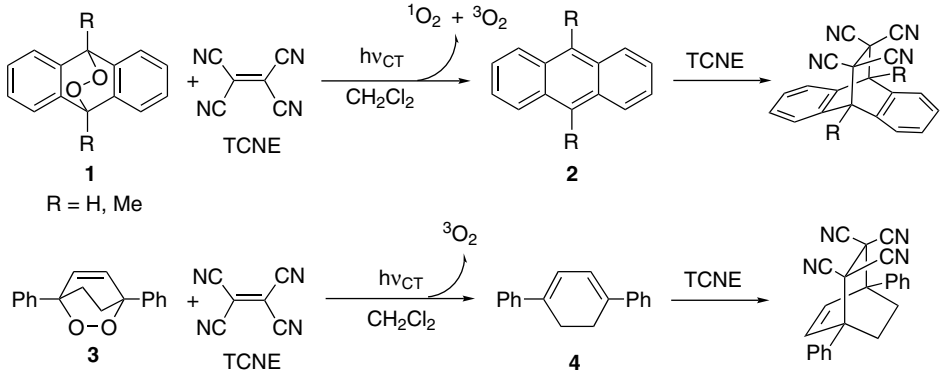
doi:10.1016/j.tetlet.2004.08.077



Scheme 1.

a proton acceptor [9] in a Pyrex tube was irradiated by a 2-kW Xe lamp (>360 nm) for 10 min, 1,4-di(*p*-methoxyphenyl)butan-1,4-dione **6a**[†,3a,10] was obtained in good yield (16% yield at 18% conversion) as the sole product (Scheme 2; entry 1 in Table 1). Prolonged irradiation (30 min) of the same solution under otherwise the same conditions increased the conversion of **5a** and the yield of **6a** (55% yield at 66% conversion: entry 2). Likewise, photosensitized reactions of **5b** and **5c** predominantly afforded the corresponding 1,4-diketones **6b** (95%) and **6c** (94%), respectively (entries 3 and 4). It seems that the low reactivity of **5a** compared to that of **5b** and **c** (entries 2–4) is ascribed to a lower oxidation potential of the *p*-anisyl group than those of the *p*-tolyl and phenyl groups. Thus, the radical ion pair, generated by the SET of **5a** with $TPPBF_4$, is likely to be deactivated by a back electron-transfer in competition with the formation of **6a** since the energy for the hole transfer from an aromatic ring to a C_4–C_5 bond is relatively higher in $\mathbf{5a}^{+\cdot}$ than that in $\mathbf{5b}^{+\cdot}$ and $\mathbf{5c}^{+\cdot}$. Detailed mechanistic studies further provided the following results. In the absence of light, **5a**–**c** were completely recovered even after 24 h. In the absence of $TPPBF_4$, only small amounts of 1,4-diketones **6a**–**c** were produced, respectively, from **5a**–**c** (2–4% yields at 4–9% conversions of **5a**–**c**). Thus, both the presence of $TPPBF_4$ and irradiation were essential to promote the degradation of **5**. The fluorescence of $TPPBF_4$ was effectively quenched by **5a**–**c**.[‡] 9,10-Dicyanoanthracene, however, was not an effective sensitizer to promote the PET reactions under the same irradiation conditions.[‡] In addition, the triplet photosensitization using benzophenone did not significantly increase the conversions of **5a**–**c** and the yields of **6a**–**c** (entries 5–7). These results would indicate that the radical cations of **5a**–**c**, generated by the SET with the excited singlet state of $TPPBF_4$, undergo elimination

[†] All products were isolated by silica gel TLC and characterized by their spectral data. The structures of **6** and **8** were also confirmed by their authentic spectral data.

Selected data for **6a**[3a,10]: colorless plates (C_2H_5OH); mp 156–157 °C; IR (KBr, cm^{-1}) 3090, 3030, 2975, 2945, 2910, 2845, 1665 (C=O), 1603, 1575, 1510; ^1H NMR (200 MHz, $CDCl_3$) δ 3.39 (s, 4H), 3.87 (s, 6H), 6.90–6.98 (m, 4H), 7.97–8.07 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 32.32 (t, 2C), 55.45 (q, 2C), 113.65 (d, 4C), 129.87 (s, 2C), 130.31 (d, 4C), 163.41 (s, 2C), 197.30 (s, 2C).

Selected data for **7a**[3a]: colorless prisms (CH_3OH); mp 70–71 °C; IR (KBr, cm^{-1}) 3030, 2960, 2850, 1713 (C=O), 1607, 1570, 1505; ^1H NMR (200 MHz, $CDCl_3$) δ 2.63 (t, 2H, J = 6.7 Hz), 2.80–2.93 (m, 2H), 3.00–3.08 (m, 2H), 3.81 (s, 3H), 5.98–6.03 (m, 1H), 6.83–6.93 (m, 2H), 7.28–7.37 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.93 (t, 1C), 38.68 (t, 1C), 39.87 (t, 1C), 55.26 (q, 1C), 113.72 (d, 2C), 119.15 (d, 1C), 126.22 (d, 2C), 133.17 (s, 1C), 136.97 (s, 1C), 158.91 (s, 1C), 210.12 (s, 1C); MS (EI) *m/z* 202 (M^+, 100%); UV λ_{max} (CH_3CN) 268.5 (ε 20,300) nm.

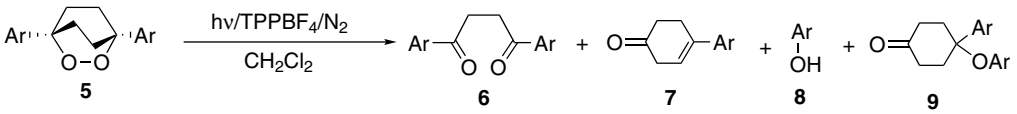
Selected data for **8a**[3a]: colorless prisms (*n*-hexane–CH_2Cl_2); mp 54–55 °C; IR (KBr, cm^{-1}) 3400 (OH), 3050, 3025, 2960, 2850, 1610, 1515; ^1H NMR (200 MHz, $CDCl_3$) δ 3.73 (s, 3H), 6.52 (br s, 1H), 6.76 (s, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 55.85 (q, 1C), 114.88 (d, 2C), 116.05 (d, 2C), 149.42 (s, 1C), 153.50 (s, 1C).

Selected data for **9a**: colorless oil; IR ($CHCl_3$, cm^{-1}) 3070, 2960, 2950, 2860, 1712 (C=O), 1617, 1590, 1502; ^1H NMR (200 MHz, $CDCl_3$) δ 2.15–2.39 (m, 4H), 2.55–2.92 (m, 4H), 3.70 (s, 3H), 3.83 (s, 3H), 6.56–6.74 (m, 4H), 6.88–6.98 (m, 2H), 7.37–7.48 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 35.79 (t, 2C), 37.13 (t, 2C), 55.26 (q, 1C), 55.51 (q, 1C), 78.55 (s, 1C), 114.03 (d, 2C), 114.14 (d, 2C), 119.82 (d, 2C), 126.56 (d, 2C), 136.31 (s, 1C), 148.87 (s, 1C), 154.19 (s, 1C), 158.91 (s, 1C), 211.12 (s, 1C).

Selected data for **10**: pale yellow needles (*n*-hexane–CH_2Cl_2); mp 121–123 °C; IR ($CHCl_3$, cm^{-1}) 3050, 2960, 1683 (C=O), 1659 (C=O), 1600, 1580, 1501; ^1H NMR (200 MHz, $CDCl_3$) δ 4.86 (s, 2H), 7.45 (s, 1H), 7.33–7.62 (m, 11H), 7.94–8.12 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 45.95 (t, 1C), 123.58 (d, 1C), 126.73 (d, 2C), 128.23 (d, 4C), 128.49 (d, 2C), 128.56 (d, 2C), 128.70 (d, 2C), 129.26 (d, 1C), 132.63 (d, 1C), 133.03 (d, 1C), 136.98 (s, 1C), 139.01 (s, 1C), 141.94 (s, 1C), 152.63 (s, 1C), 190.70 (s, 1C), 195.97 (s, 1C).

Selected data for **11b**: colorless crystalline; IR ($CHCl_3$, cm^{-1}) 3080, 2960, 1709 (C=O), 1510, 1443, 1412, 1320, 1255, 1177, 1135, 1107; ^1H NMR (200 MHz, $CDCl_3$) δ 2.00–2.21 (m, 2H), 2.24–2.47 (m, 2H), 2.36 (s, 3H), 2.68–2.88 (m, 2H), 3.08 (s, 3H), 7.15–7.25 (m, 2H), 7.28–7.36 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 21.02 (q, 1C), 34.95 (t, 2C), 50.27 (q, 1C), 75.91 (s, 1C), 125.81 (d, 2C), 129.14 (d, 2C), 137.18 (s, 1C), 140.06 (s, 1C), 211.46 (s, 1C).

[‡] The oxidation potentials of **5a**–**c** were measured by cyclic voltammetry at v = 100 mV sec^{-1} in CH_3CN containing 0.1 M Et_4NClO_4 ($E^{ox}_{1/2}$/V vs SCE: 1.72, 2.08, and 2.08, respectively, for **5a**–**c**) and found to be low enough to quench the excited singlet state of $TPPBF_4$ ($E^*_{red}(S_1) \approx 2.5$ V vs SCE).[8] Indeed, **5a**–**c** effectively quenched the fluorescence of $TPPBF_4$ ($k_q\tau$ = 76.8, 54.4, 44.7 in CH_2Cl_2, respectively, for **5a**–**c**). On the contrary, the fluorescence of DCA ($E^*_{red}(S_1) \approx 1.9$ V vs SCE)[11] was not measurably quenched by **5b** and **5c** but was quenched by **5a**. DCA-sensitized photoreactions of **5a**–**c** (DCA = 1.0×10^{-2} mmol; 2 kW Xe lamp; λ > 360 nm; irradiated for 30 min.) produced the corresponding diketones **6a**–**c** (2–4% yields at 3–9% conversions of **5a**–**c**) as the sole product.



Scheme 2.

Table 1. $TPPBF_4$-sensitized PET reactions of 1,4-diaryl-2,3-dioxabicyclo[2.2.2]octanes **5**[a]

Entry	5	Sensitizer/conditions	Time (min)	Conv. (%)	Yield (%)[b]			
					6	7	8	9
1	**5a**	$TPPBF_4$/DTBP[c]	10	18	16(88)[d]	0	0	0
2	**5a**	$TPPBF_4$/DTBP[c]	30	66	55(83)[d]	0	0	0
3	**5b**	$TPPBF_4$/DTBP[c]	30	100	95	0	0	0
4	**5c**	$TPPBF_4$/DTBP[c]	30	100	94	0	0	0
5	**5a**	BP[e]	30	22	13	0	0	0
6	**5b**	BP[e]	30	14	9	0	0	0
7	**5c**	BP[e]	30	10[f]	10	0	0	0
8	**5a**	$TPPBF_4$[g]	5	38	<1	18	23	15
9	**5a**	$TPPBF_4$[g]	10	100	2	74	97	0
10	**5b**	$TPPBF_4$[g]	30	54	7[f]	9[f]	30	17[f]
11	**5c**	$TPPBF_4$[g]	30	19	16	0	0	0

[a] Irradiated by a 2-kW Xe lamp (>360 nm); 20–21 °C; **5** = 2.0×10^{-1} mmol; CH_2Cl_2 = 10 mL.
[b] Isolated yield by silica gel TLC.
[c] $TPPBF_4$ = 1.0×10^{-2} mmol; DTBP: di-*tert*-butylpyridine = 1.0×10^{-2} mmol.
[d] Conversion yield.
[e] Irradiated by a 2-kW Xe lamp (>340 nm) in the presence of BP; BP: benzophenone = 2.0×10^{-1} mmol.
[f] Determined by 200 MHz ^{1}H NMR.
[g] $TPPBF_4$ = 1.0×10^{-2} mmol.

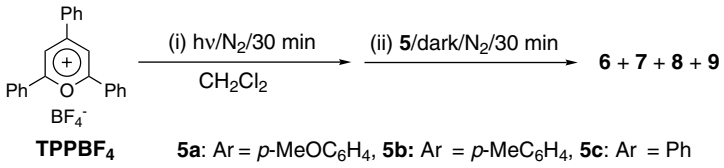
of ethylene, *not molecular oxygen*!,[6a–c] to give the corresponding 1,4-diketones **6a–c**.

Interestingly, when $TPPBF_4$-sensitized photoreaction of **5a** was performed in the absence of DTBP, 4-(*p*-methoxyphenyl)cyclohex-3-en-1-one **7a**[4a], *p*-methoxyphenol **8a**[3a], and 4-(*p*-methoxyphenyl)-4-(*p*-methoxyphenyl)-oxycyclohexanone **9a** were obtained along with a small amount of 1,4-di(*p*-methoxyphenyl)butan-1,4-dione **6a**[3a,10] (entry 8).† Prolonged irradiation (10 min) of the same solution under otherwise the same conditions resulted in complete conversion of **5a** and degradation of **9a** to afford **7a** and **8a** along with a small amount of **6a** (entry 9). These products are probably produced through acid-catalyzed pathways.§ Likewise, the photoreaction of **5b** afforded **6b**, **7b**, **8b**, and **9b** under the same irradiation conditions (entry 10). However, diketone **6c** was the sole product from **5c** (entry 11). These results suggest that a cationic intermediate such as **14** (see Scheme 4) is involved in these reactions and an *O*-1,2-aryl shift in **14** is promoted by electron-donating aromatic groups (*p*-An > *p*-Tol). DTBP probably acts as a proton acceptor to interfere with the generation of **14**. On the other hand, DTBP may also act as a co-sensitizer[12] since the PET reactions of **5b** and **5c** (entries 3–4) were significantly accelerated by the addition of DTBP compared to those without DTBP (entries 10 and 11). Judging from the oxidation potential of DTBP ($E^{ox}_{1/2}$ = 2.27 V vs. SCE) and the fluorescence quenching of $TPPBF_4$ by DTBP ($k_q\tau$ = 37.0 M^{-1} in CH_3CN), it is possible that DTBP can act as a co-sensitizer.

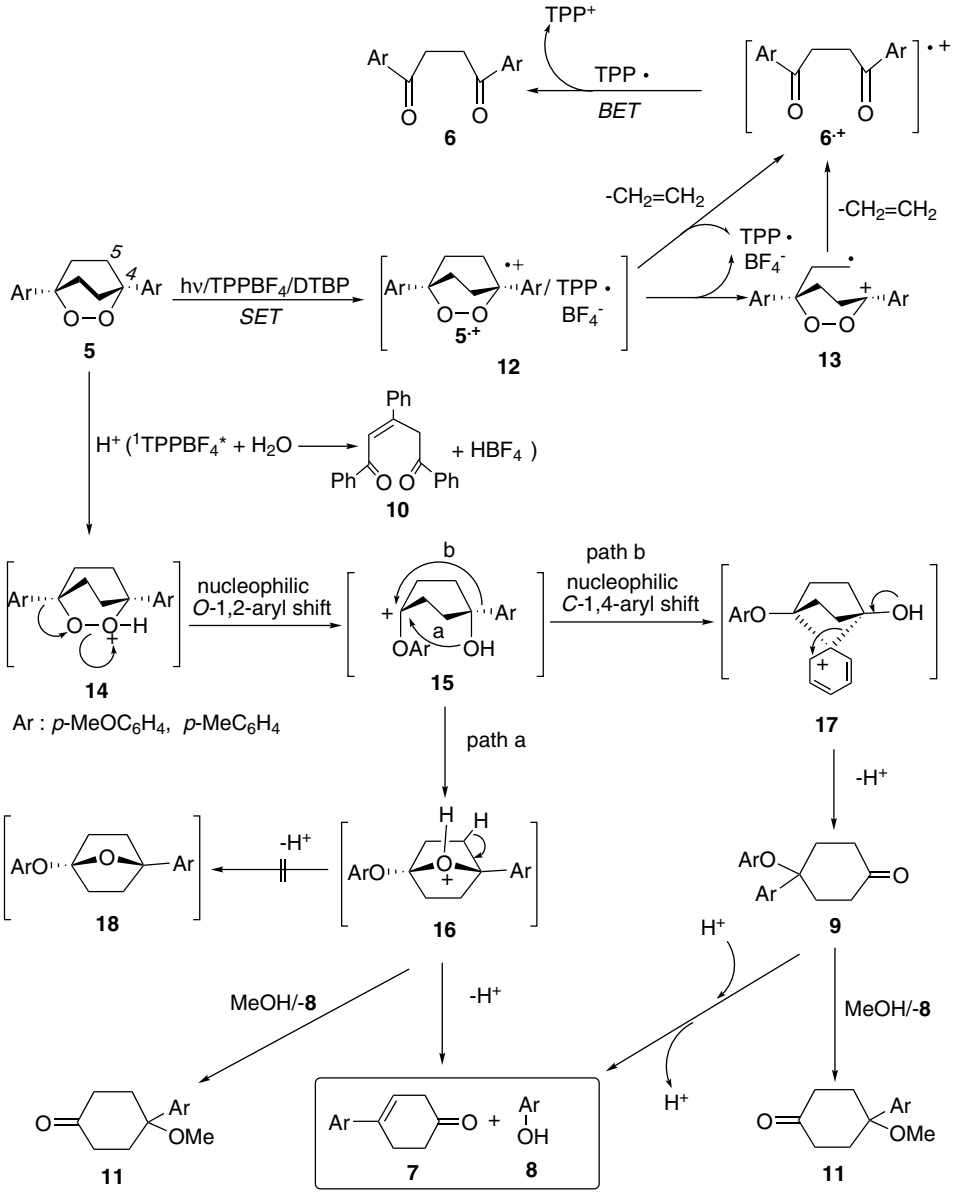
The above results indicate that both the SET and the acid-catalyzed pathways concurrently operate in the $TPPBF_4$-induced PET reactions, and that **6** was produced through the SET pathway, whereas **7**, **8**, and **9** were produced through the acid-catalyzed pathways that are completely suppressed by the addition of DTBP.

In order to ascertain the production of an acidic species under the irradiation conditions, a nitrogen-purged CH_2Cl_2 solution of $TPPBF_4$ (without **5**) was irradiated for 30 min, and successively, **5a** was added to the resultant photolysate and the resultant solution was further stirred for 30 min in the dark. As a result, **5a** was completely converted to **7a** and **8a** (Scheme 3, entry 1 in Table 2). Similar treatment of **5b** resulted in slight degradation to give **7b**, **8b**, and **9b**, whereas **5c** was almost inert (entries 2 and 3 in Table 2). Notably, about 20% of $TPPBF_4$ was decomposed to give 1,3,5-triphenylpent-2-en-1,5-dione **10**† during irradiation (30 min), as determined by UV measurements of the absorption maxima of $TPPBF_4$ before and after irradiation. These results would indicate that the excited state of $TPPBF_4$ ($TPPBF_4^*$) produces an acidic species such as HBF_4, which might be formed by the reaction of $TPPBF_4^*$ with moisture in the solution. To ascertain the catalytic ability of HBF_4, reactions of **5a–c** with HBF_4 were tested. Actually, a catalytic amount of HBF_4 (0.2 mol% to **5a**) in MeOH effectively promoted the rearrangement and

§ Although the generation of an acidic species in the PET reactions using $TPPBF_4$ in CH_2Cl_2 has been suggested, the reaction mechanism was not completely elucidated.[8k,l]



Scheme 3.



Scheme 4.

fragmentation of **5a** to give **7a** (50%), **8a** (85%), **9a** (6%), and 4-methoxy-4-(*p*-methoxyphenyl)cyclohexanone **11a** (22%), respectively. Although **5b** was almost inert with the same amount of HBF_4 (0.2 mol% to **5b**), treatment of **5b** with a larger amount of HBF_4 (1.0 mol% to **5b**) gave **8b** (24%), **9b** (2%), and **11b**[†] (21%), at 43% conversion of **5b**. On the other hand, **5c** was almost inert even with a larger amount of HBF_4 (up to 2.0% to **5c**). These results are consistent with those by the TPP-sensitized PET reactions of **5a–c** in the absence of DTBP (entries 8–11).

On the basis of the above results, a reasonable mechanism for the rearrangement and fragmentation of **5** is proposed in Scheme 4. The SET from **5** to the excited singlet state of $TPPBF_4$ ($^1TPPBF_4^*$) generates the radical ion pair **12** composed of the radical cation $\mathbf{5}^{+\cdot}$ and $TPP^{\cdot}$. The radical cation $\mathbf{5}^{+\cdot}$ undergoes C_4–C_5 bond cleavage

Table 2. Reactions of 1,4-diaryl-2,3-dioxabicyclo[2.2.2]octanes **5** with the photolysate of $TPPBF_4$ in CH_2Cl_2

Entry	Condition	Conv. (%)	Yield (%)[a]			
			6	**7**	**8**	**9**
1	(i) hν/$TPPBF_4$/30 min[b]; (ii) **5a**/dark/30 min[c]	100	0	91	97	0
2	(i) hν/$TPPBF_4$/30 min[b]; (ii) **5b**/dark/30 min[c]	15	0	<1	6	4
3	(i) hν/$TPPBF_4$/30 min[b]; (ii) **5c**/dark/30 min[c]	5	0	0	0	0

[a] Isolated yield by silica gel TLC.
[b] Irradiated by a 2-kW Xe lamp (>360 nm) under N_2 atmosphere; 20–21 °C; $TPPBF_4 = 1.0 \times 10^{-2}$ mmol; $CH_2Cl_2 = 10$ mL.
[c] Compound **5** (2.0×10^{-1} mmol) was added to the photolysate of (i) and the solution was stirred for 30 min in the dark.

to generate the radical cation **13** followed by elimination of ethylene to form $\mathbf{6}^{+\cdot}$.[¶] The radical cation $\mathbf{6}^{+\cdot}$ thus formed produces the diketone **6** upon a back electron-transfer (BET) from $TPP^{\cdot}$.[‖] It is also possible that the radical cation $\mathbf{6}^{+\cdot}$ is generated directly from the radical cation $\mathbf{5}^{+\cdot}$ through the simultaneous C_4–C_5 and O–O bond cleavages.

On the other hand, **5** is protonated by HBF_4, which is photochemically produced from the reaction of $TPPBF_4^*$ with H_2O, to generate the hydroxonium **14**. The hydroxonium **14** undergoes a nucleophilic *O*-1,2-aryl shift[2f,3a,c] to form the carbocation **15**. As for the rearrangement and fragmentation from **15**, two reaction pathways might be considered. One is the formation of the bicyclic intermediate **16** by an intramolecular hydroxyl addition to the carbocation in **15** (path a). The other is the formation of the bicyclic intermediate **17** by an intramolecular nucleophilic aryl addition (*C*-1,4-aryl shift)[**] to the carbocation in **15** (path b). The intermediate **16** undergoes fragmentation to give **7** and **8** rather than producing the strained bicyclic acetal **18**, whereas the intermediate **17** rearranges to give the keto-ether **9** followed by the proton-catalyzed fragmentation to give **7** and **8**. The aryl migration to give **15** and **9** is promoted by electron-donating *p*-substituents on the phenyl ring (*p*-An > *p*-Tol≫Ph), as observed in the proton-catalyzed reactions of **5a**–**c**. In the reactions of **5a**–**c** with the HBF_4-MeOH solution, the formation of **11a** and **11b** could be explained by a nucleophilic attack of MeOH to **9** and/or **16**.

In summary, we have demonstrated that: (i) $TPPBF_4$ is an effective PET sensitizer to generate the radical cations of **5a**–**c**; (ii) **5a**–**c** underwent novel SET fragmentation through their radical cations to afford ethylene and 1,4-diarylbutan-1,4-diones **6**, whereas **5** concurrently underwent novel proton-catalyzed rearrangement and fragmentation to afford 4-aryl-4-aryloxycyclohexanones **9**, 4-aryl-cyclohex-3-en-1-ones **7**, and *p*-substituted phenols **8**; (iii) the evidence for the nucleophilic *O*-1,2-aryl shifts[2f] and the novel nucleophilic *C*-1,4-aryl shifts was obtained by the isolation of rearrangement products **9a** and **9b**; (iv) the SET and the proton-catalyzed pathways were distinguished by using 2,6-di-*tert*-butylpyridine (DTBP) as a proton acceptor. We are conducting further studies on the PET and the proton-catalyzed reactions of cyclic peroxides to clarify their reactivity and mechanisms.

[¶] If the charge and spin are localized around the O–O bond, $\mathbf{5}^{+\cdot}$ would not undergo the O–O bond cleavage since such O–O bond possesses a double bond character.[5,6a]

[‖] At the present stage, it cannot be completely ruled out that the triplet excited state of **5**, generated by a back electron-transfer within the radical ion pair **12**, would produce **6**.

[**] A transannular 1,4-*C*-aryl shift has been observed in a 4,4-diphenylcyclohexyl radical system, whereas analogous cationic 1,4-*C*-aryl shifts are unknown in the same system.[13]

Acknowledgements

We are grateful to Prof. Eietsu Hasegawa (Faculty of Science, Niigata University), Prof. Tsutomu Miyashi and Dr. Hiroshi Ikeda (Faculty of Science, Tohoku University) for their helpful comments and assistance. This work was partially supported by a grant from The Uchida Energy Science Promotion Foundation.

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