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Chemical capture of an unprecedented oxatetramethyleneethane radical cation with a through-space electronic coupling

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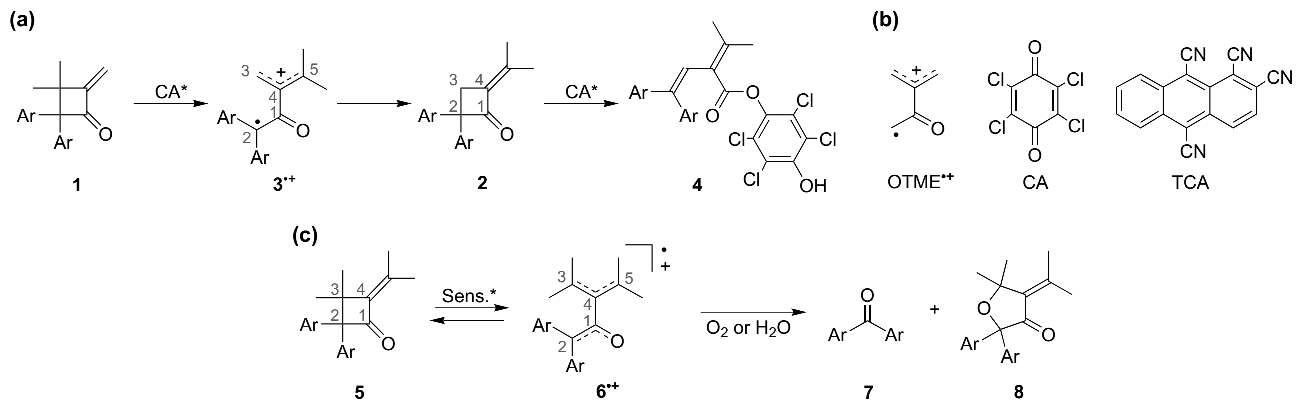
Abstract—A photoinduced electron-transfer reaction of 2,2-dianisyl-4-isopropylidene-3,3-dimethylcyclobutanone (**5**) in acetonitrile containing molecular oxygen or water gave 4,4′-dimethoxybenzophenone (**7**) and 2,2-dianisyl-4-isopropylidene-5,5-dimethyl-dihydrofuran-3-one (**8**), demonstrating the chemical capture of an unprecedented oxatetramethyleneethane-type radical cation intermediate ($\mathbf{6}^{\cdot+}$). A density functional theory calculation suggests through-space electronic coupling between the tetramethylallyl and joined dianisylmethyl carbonyl subunits in $\mathbf{6}^{\cdot+}$.

Recently, we reported on a novel rearrangement of 2,2-dianisyl-3,3-dimethyl-4-methylenecyclobutanone (**1**, Scheme 1a) to give 2,2-dianisyl-4-isopropylidenecyclobutanone (**2**), triggered by a photoinduced electron-transfer (PET) reaction using *p*-chloranil (CA, Scheme 1b).[1] The reaction proceeded irreversibly via an unprecedented oxatetramethyleneethane radical cation (OTME$^{\cdot+}$, Scheme 1b) derivative, $\mathbf{3}^{\cdot+}$, which is a new category of non-Kekulé molecules. Unfortunately, however, we did not succeed in capturing a distonic radical cation $\mathbf{3}^{\cdot+}$ with ylophilic and nucleophilic trapping reagents, such as molecular oxygen[2] and methanol[3] or water,[3] respectively. This may be attributed to low stationary concentration of $\mathbf{3}^{\cdot+}$, which is caused by irreversibility between **1** and **2**; **2** did not undergo C-2–C-3 bond cleavage, but underwent C-1–C-2 bond cleavage to give CA-adduct **4** under the CA sensitized PET conditions. Another OTME$^{\cdot+}$-type intermediate $\mathbf{6}^{\cdot+}$ can be efficiently generated from the radical cation of 2,2-dianisyl-4-isopropylidene-3,3-dimethylcyclobutanone (**5**, Scheme 1c)



Scheme 1. (a) PET reactions of **1** and **2**. (b) The parent OTME^{+} and sensitizers. (c) PET reactions of **5** in acetonitrile. Ar = 4-MeOC$_6$H$_4$.

Keywords: Photochemistry; Electron transfer; Oxatetramethyleneethane; Methylenecyclobutanone; Radical cation; Electronic coupling.

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by constructing a reversible (degenerate) rearrangement system. In addition, a steric repulsion between the geminal dianisyl and dimethyl groups at C-2 and C-3 of $6^{\cdot+}$ can extend the lifetime of $6^{\cdot+}$ compared with that of $3^{\cdot+}$. Expecting to capture an OTME$^{\cdot+}$-type intermediate, in this work, we studied PET reactions of **5** in acetonitrile containing molecular oxygen or water, and found that $6^{\cdot+}$ was captured by molecular oxygen and water at the same C-2 position to give 4,4′-dimethoxybenzophenone (**7**) and 2,2-dianisyl-4-isopropylidene-5,5-dimethyldihydrofuran-3-one (**8**). Here, we briefly report on the chemical capture of $6^{\cdot+}$ and its unique electronic structure using product analyses and a density functional theory (DFT) calculation.

Ketone **5** was prepared in 73% yield by the [2 + 2] cycloaddition of dianisylketene and 2,4-dimethylpentan-2,3-diene (1,1,3,3-tetramethylallene) using known procedures.[1,4,5] The X-ray crystallographic analysis of **5**[6] reveals that the C-2–C-3 bond of **5** is 1.62 Å long (Fig. 1a). In comparison with a normal C(sp^3)–C(sp^3) bond (1.54 Å), the C-2–C-3 bond is lengthened by steric repulsion between the geminal dianisyl and dimethyl groups at C-2 and C-3, respectively. Therefore, **5** readily cleaves to $6^{\cdot+}$ on oxidation by PET.[1b] On irradiation (2 kW xenon lamp, $\lambda > 440$ nm)[7] for 30 min at 20 °C in degassed dry acetonitrile with CA ($E_{1/2}^{\mathrm{red}} = \pm 0.00$ V vs SCE in acetonitrile), considerable ketone **5** ($E_{\mathrm{ap}}^{\mathrm{ox}} = +1.43$ V) was consumed (30%), but no identifiable product was observed (Table 1). Under similar PET conditions, but with an oxygen atmosphere, **7** was formed in 59% yield at 62% conversion (Scheme 2). By contrast, on similar irradiation for 60 min in degassed aqueous [2% (v/v)] acetonitrile, **8**,[8] and 2,3,5,6-tetrachlorohydroquinone (CAH$_2$) were formed in 68% and 50% yields, respectively, at 68% conversion. The structure of **8** was determined by X-ray crystallography (Fig. 1b).[6] The formation of **7** and **8** occurred concurrently in the presence of both molecular oxygen and water. In acetonitrile containing methanol [2% (v/v)], no identifiable product was observed. Changing the sensitizer to 1,2,9,10-tetracyanoanthracene (TCA, Scheme 1b, $E_{1/2}^{\mathrm{red}} = -0.43$ V)[9] **5** gave **7** in degassed aqueous [4% (v/v)] acetonitrile in 40% yield at 40% conversion or in dry acetonitrile under oxygen in moderate yield. In addition, **8** was not consumed in a similar PET reaction in degassed aqueous [4% (v/v)] acetonitrile for 30 min.

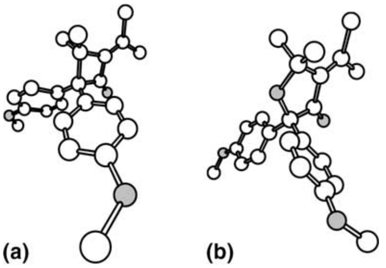
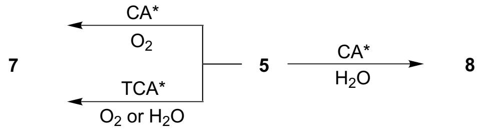


Figure 1. The ORTEP drawings of (a) **5** and (b) **8**. Hydrogen atoms are omitted for clarity.



Scheme 2. PET reactions of **5** in acetonitrile.

The product analyses suggest that two electronic structures contribute to the reactivity of the OTME$^{\cdot+}$ derivative $6^{\cdot+}$; type A (**6**-A$^{\cdot+}$) with the dianisylmethyl radical and the tetramethylallyl cation subunits, and type B (**6**-B$^{\cdot+}$), the counterpart of type A (Scheme 3). Note that ylophilic and nucleophilic additions of molecular oxygen and water, respectively, are suggested to take place in the same C-2 position of $6^{\cdot+}$. Therefore, $6^{\cdot+}$ does not behave as a simple distonic radical cation like $3^{\cdot+}$, but behaves just like a non-distonic radical cation with two equivalent resonance structures, types A and B. Efficient electronic coupling[10] probably operates in $6^{\cdot+}$ (vide infra).

A plausible reaction mechanism for the PET reactions of **5** is depicted in Scheme 3. The $5^{\cdot+}$ initially formed as a free radical ion (or in a solvent-separated radical ion pair) undergoes C-2–C-3 bond cleavage to give the OTME$^{\cdot+}$ derivative $6^{\cdot+}$. The ylophilic addition of molecular oxygen[11] to the C-2 site of $6^{\cdot+}$ (cf. **6**-A$^{\cdot+}$) gives ketone **7** via radical $11^{\cdot}$. Conversely, the nucleophilic addition of water to the C-2 site of $6^{\cdot+}$ (cf. **6**-B$^{\cdot+}$) fol-

Table 1. PET reactions of **5** in acetonitrile[a]

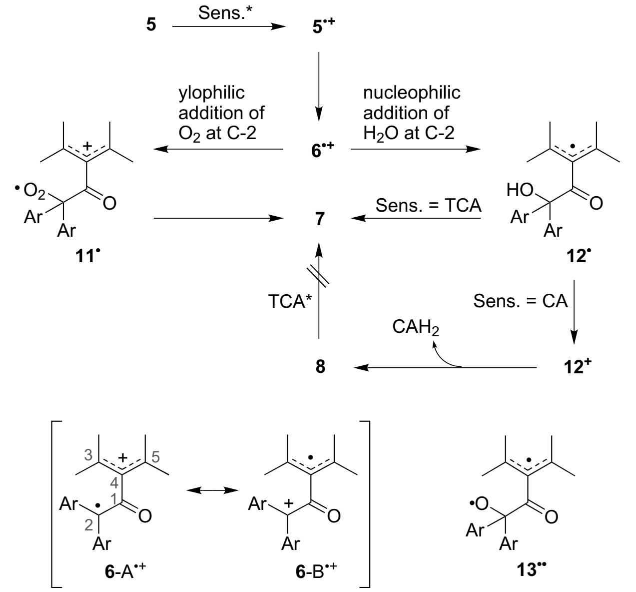
Sens.	Atmosphere	H$_2$O% (v/v)	Time (min)	Conv.[b]	Yields[b]	
					7	**8**
CA	Degassed	0	30	30	0	0
	Oxygen	0	20	62	59	0
	Degassed	2	60	68[c]	0	68
	Oxygen	2	20	80	57	23
TCA	Degassed	0	30	5	[d]	0
	Oxygen	0	60	40	25	0
	Degassed	4	60	40	40	0

[a] [**5**] = [CA] = 0.01 M, [TCA] = 0.002 M.

[b] The conversions and yields were determined by ^{1}H NMR analysis and are given in %.

[c] CAH$_2$ was isolated in 50% yield.

[d] A trace amount (<2%) of **7** was detected.



Scheme 3. A plausible reaction mechanism for the PET reactions of **5**.

lowed by deprotonation, gives radical **12**$^{\bullet}$ and CAH$^{\bullet}$ or TCAH$^{\bullet}$. When the sensitizer is CA, **8** is given by a secondary electron transfer (with CAH$^{\bullet}$)-cyclization sequence via **12**$^{+}$. Another pathway via **13**$^{\bullet\bullet}$, which is formed by hydrogen abstraction in **12**$^{\bullet}$ by CAH$^{\bullet}$, may also be possible in the formation of **8**. Ketone **7** observed in the PET reaction with TCA in degassed aqueous acetonitrile must be formed from **12**$^{\bullet}$, as **7** was not formed from **8** under similar PET conditions. The difference in the reactivity of **12**$^{\bullet}$ between the CA- and TCA-sensitization may be ascribed to lower efficiency of the secondary electron transfer from **12**$^{\bullet}$ to TCAH$^{\bullet}$ compared with CAH$^{\bullet}$. Unfortunately, we have no details on the fragmentation of **11**$^{\bullet}$ to **7** because we could not identify any other product(s) except **7** in the CA-sensitized PET reactions of **5** under oxygen or in the TCA-sensitized PET reactions of **5**. However, the formation of **7** and **8** and mechanistic conjecture strongly suggests the chemical capture of **6**$^{\bullet+}$ with ylophilic molecular oxygen and nucleophilic water at the same C-2 position. An alternative explanation is a distonic radical cation model that involves either type A (**6**-A$^{\bullet+}$) or B (**6**-B$^{\bullet+}$) as a real intermediate. For example, ylophilic and nucleophilic addition of molecular oxygen and water to the C-2 carbon of **6**-A$^{\bullet+}$ would give **7** and **8**, respectively. However, this pathway seems unlikely because it is impossible to explain the formation of **7** in the PET reaction of **5** with TCA in degassed aqueous acetonitrile. Note that **8** did not give **7** under similar PET conditions.

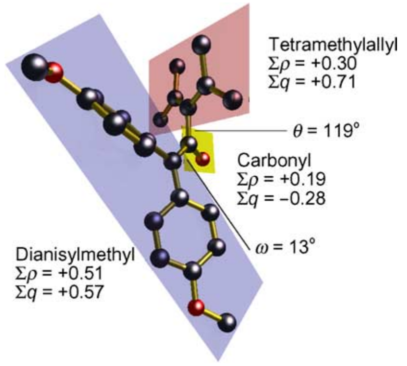


Figure 2. Definition of three subunits in the framework of **6**$^{\bullet+}$, calculated dihedral angles (θ and ω), and the sum of the partial spin and charge densities ($\Sigma\rho$ and Σq) on the optimized structure (hydrogen atoms are omitted for clarity) obtained from UB3LYP/6-31G calculations.

Moreover, the UB3LYP/6-31G calculation[13] suggests electronic coupling in **6**$^{\bullet+}$. Figure 2 defines three subunits in the framework of **6**$^{\bullet+}$, the calculated dihedral angles (θ and ω), and the sum of the partial spin and charge densities ($\Sigma\rho$ and Σq); there was no significant difference in $\Sigma\rho$ or Σq between the dianisylmethyl and tetramethylallyl subunits. The spin and charge are delocalized all over the molecule. The tetramethylallyl and carbonyl planes are largely twisted with respect to each other ($\theta = 119°$), whereas the carbonyl and dianisylmethyl subunits are almost in the same plane ($\omega = 13°$). The resulting bisected conformation favors a through-space electronic coupling[16] between the tetramethylallyl and jointed dianisylmethyl carbonyl subunits. Note that the π-orbitals at the C-3 and C-5 are in phase with that at the C-2 and the carbonyl oxygen, as exemplified by the SOMO (α) of **6**$^{\bullet+}$ (Fig. 3). Needless to say, no similar electronic coupling is observed for the parent planar OTME$^{\bullet+}$ and slightly bisected **3**$^{\bullet+}$ (for the C-1–C-4),[1a] but may be observed for the perpendicular tetramethyleneethane radical cation.[17] Obviously, the deviation from the planar structure of **6**$^{\bullet+}$ is due to steric hindrance between the tetramethylallyl and dianisylmethyl subunits.

In conclusion, we succeeded in the chemical capture of the OTME$^{\bullet+}$ derivative **6**$^{\bullet+}$, which is suggested to be trapped with molecular oxygen and water at the same carbon, C-2. DFT calculations demonstrate the efficient through-space electronic coupling in **6**$^{\bullet+}$, whose electronic structure can be depicted as a resonance hybrid of two equivalent resonance structures: types A and B. This work provides a new perspective on radical ions and non-Kekulé chemistry, and will affect the related fields of reactive intermediate and organic photochemistry. Further studies are now in progress, and will be published elsewhere.[18]

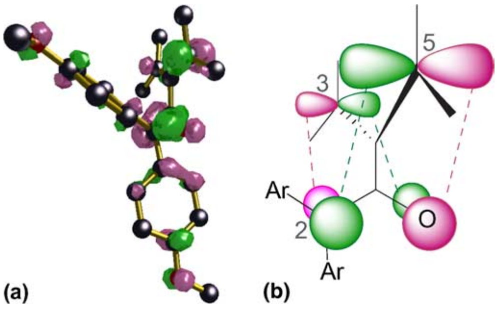


Figure 3. (a) Representation of the SOMO (α) of **6**$^{\bullet+}$. A similar figure was obtained for the SOMO (β). (b) Conceptual representation, indicating the electronic coupling of the two terminal allylic carbons (C-3 and C-5), dianisylmethyl carbon (C-2), and carbonyl oxygen.

Acknowledgements

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Supplementary data

Estimation of free energy changes for electron transfer from **5** to the excited state of sensitizers, X-ray crystallography for **5** and **8**, and the calculation results of **6**$^{\cdot+}$ (PDF). These material are available free of charge via the Internet at http://www.sciencedirect.com. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.02.109.

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5. Selected data for **5**: mp 129.0 °C (colorless needles from ethanol); IR (KBr) 1717 cm^{-1}; MS (EI, 70 eV) *m/z* (relative intensity): 351 (21), 350 (85, M$^+$), 268 (30), 254 (47), 242 (45), 228 (10), 227 (66), 226 (100, Ar$_2$C$^{\cdot+}$), 211 (27); ^{1}H NMR (200 MHz, CDCl$_3$) δ_{ppm} 1.27 (s, 6H), 1.86 (s, 3H), 2.23 (s, 3H), 3.77 (s, 6H), 6.81 (AA′BB′, J = 9.0 Hz, 4H), 7.32 (AA′BB′, J = 9.0 Hz, 4H); ^{13}C NMR (50 MHz, CDCl$_3$) δ_{ppm} 20.26, 22.23, 26.49 (2C), 46.77, 55.12 (2C), 76.26, 113.33 (4C), 129.26 (4C), 133.49 (2C), 144.37, 147.67, 157.97 (2C), 203.05; Anal. Calcd for C$_{23}$H$_{26}$O$_3$: C, 78.83; H, 7.48. Found: C, 78.96; H, 7.51.
6. Crystallographic data for **5** and **8** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication nos. CCDC 252673 (**5**) and 241921 (**8**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
7. The procedure used for the PET reactions of **5** is as follows. An acetonitrile solution (5 mL) containing **5** (17.5 mg, 0.05 mmol), CA (12.3 mg, 0.05 mmol) or TCA (2.8 mg, 0.01 mmol), and water (0, 0.1, or 0.2 mL) in a Pyrex test tube (diameter 1.5 cm) was degassed with five freeze (−196 °C)–pump (10^{-2} Torr)–thaw (ambient temperature) cycles and then sealed at 10^{-2} Torr. An oxygen-saturated solution was prepared by successive bubbling with oxygen for 10 min and then sealed under an oxygen atmosphere. The sample solution was irradiated through a cutoff filter ($\lambda > 440$ nm) with a 2 kW xenon lamp at 20 ± 1 °C. After evaporation in vacuo, the product yields were determined by ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane as the internal standard for integration.
8. The procedure for isolating **8** is as follows. An acetonitrile solution (33 mL) containing **5** (231 mg, 0.66 mol), CA (391 mg, 1.32 mmol), and water (1 mL) in a large cylindrical quartz cell (diameter 2.0 cm) was irradiated through a cutoff filter ($\lambda > 440$ nm) with a 2 kW xenon lamp at 20 ± 1 °C under an argon atmosphere for 3 h. After evaporation in vacuo, column chromatography followed by recrystallization from ethanol gave 110 mg (0.30 mmol, 46% yield) of **8**. Selected data for **8**: mp 121.0–121.5 °C (colorless prisms); IR (KBr) 1703 cm^{-1}; MS (EI, 70 eV) *m/z* (relative intensity): 367 (5), 366 (20, M$^+$), 243 (11), 135 (25), 124 (73), 96 (100, (CH$_3$)$_2$CCC(CH$_3$)$_2^{\cdot+}$), 81 (30); ^{1}H NMR (600 MHz, CDCl$_3$) δ_{ppm} 1.52 (s, 6H), 1.98 (s, 3H), 2.32 (s, 3H), 3.77 (s, 6H), 6.82 (AA′BB′, J = 8.7 Hz, 4H), 7.36 (AA′BB′, J = 8.7 Hz, 4H); ^{13}C NMR (150 MHz, CDCl$_3$) δ_{ppm} 22.14, 23.95, 28.96 (2C), 55.19 (2C), 81.06, 86.52, 113.32 (4C), 128.05 (4C), 135.02, 135.33 (2C), 152.21, 158.77 (2C), 202.22; Anal. Calcd for C$_{23}$H$_{26}$O$_4$: C, 75.38; H, 7.15. Found: C, 75.10; H, 7.20.
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18. Further product analysis using GC–MS are needed for the complete elucidation of the reaction mechanism. We are now studying this and will publish the results separately.