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# Significant solvent effects and unusual additions of *p*-chloranil in the photoinduced electron-transfer reaction of 2,2-dianisyl-4-isopropylidene-3,3-dimethylcyclobutanone

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This paper is dedicated to Emeritus Professor T. Miyashi on the occasion of his retirement from Tohoku University

**Abstract**—A photoinduced electron-transfer reaction of 2,2-dianisyl-4-isopropylidene-3,3-dimethylcyclobutanone (**1**) in benzene gave two unexpected CA-adducts, 5,5-dianisyl-4,4-dimethyl-3-[1-(4-hydroxy-2,3,5,6-tetrachlorophenyl)methylethylidene]dihydrofuran-2-one (**7**) and 2,2-dianisyl-4-(4-hydroxy-2,3,5,6-tetrachlorophenoxy)-4-isopropenyl-3,3-dimethylcyclobutanone (**8**), while the reaction in acetonitrile did not, suggesting significant solvent effects on the product distribution.

Recently, we reported the first chemical capture of the radical cation variant of the oxatetramethyleneethane (3-methylenebutan-2-one-1,4-diyl radical cation, OTME$^{\cdot+}$, Chart 1) intermediate.[1] Photoinduced electron-transfer (PET) reactions of 2,2-dianisyl-4-isopropylidene-3,3-dimethylcyclobutanone [**1**, anodic peak potential $(E^{\text{ox}}_{\text{ap}}) = +1.43$ V versus SCE, in acetonitrile] using *p*-chloranil (CA, $E^{\text{red}}_{1/2} = \pm 0.00$ V) or 1,2,9,10-tetracyanoanthracene (TCA, $-0.43$ V)[2] generated an OTME$^{\cdot+}$-type intermediate **2**$^{\cdot+}$, which was captured by water[3] or molecular oxygen[5] in acetonitrile to give 2,2-dianisyl-4-isopropylidene-5,5-dimethyldihydrofuran-3-one (**3**) and

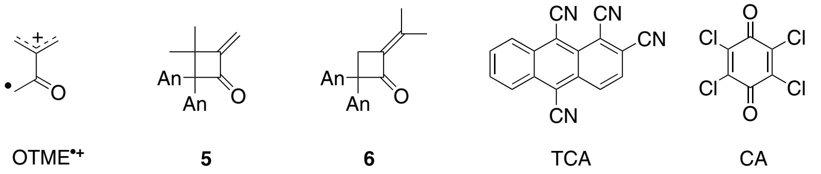
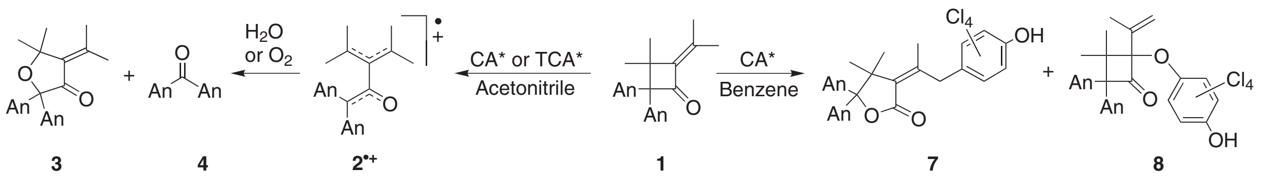


**Chart 1.** The parent OTME$^{\cdot+}$, 2-methylenecyclobutanone derivatives and sensitisers. An = $4\text{-MeOC}_6\text{H}_4$.



**Scheme 1.** Solvent- and sensitiser-dependent PET reactions of **1**.

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*Keywords*: Photochemistry; Electron transfer; Methylenecyclobutanone; Radical cation; Addition reaction; Solvent effects; Oxatetramethyleneethane.

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4,4′-dimethoxybenzophenone (**4**, Scheme 1).[1] Interestingly, similar PET reactions of the 2-methylenecyclobutanone derivatives, **5** and **6**, strongly depend on the solvents and sensitisers.[7–9] A CA-sensitised PET rearrangement from **5** to **6** via the corresponding OTME$^{\cdot+}$-type intermediate took place efficiently in nonpolar benzene, but not in polar acetonitrile, while similar TCA-sensitised photoreactions in both solvents resulted in the formation of a complex mixture. To gain further insight into the reactivity of $\mathbf{1}^{\cdot+}$, we studied solvent effects on the CA- or TCA-sensitised PET reactions of **1**. Here, we briefly report on the significant solvent and sensitiser effects on the product distribution and the occurrence of unexpected CA addition reactions.[10]

PET reactions of **1** were carried out with a 2 kW Xe lamp ($\lambda > 440$ nm). Methylenecyclobutanone **1** was not consumed on irradiation of TCA for 60 min at 20 °C in degassed dry benzene with or without water or molecular oxygen. Similar irradiation of CA for 30 min in degassed dry acetonitrile resulted in the sole consumption of **1** (30%, Table 1).[1] Conversely, a similar reaction in degassed dry benzene for 60 min gave two unexpected CA-adducts, 5,5-dianisyl-4,4-dimethyl-3-[1-(4-hydroxy-2,3,5,6-tetrachlorophenyl)methylethylidene]dihydrofuran-2-one (**7**, Scheme 1) and 2,2-dianisyl-4-(4-hydroxy-2,3,5,6-tetrachlorophenoxy)-4-isopropenyl-3,3-dimethylcyclobutanone (**8**) in 27% and 16% yields, respectively, at 49% conversion. [13] A small amount of **7** was detected under PET conditions in dry dichloromethane. The structure of **7** was determined in X-ray crystallographic analyses, and is shown in Figure 1.[14] The structure of **8** was confirmed by spectroscopic analyses,[13] especially $^1$H NMR analyses involving heteronuclear single quantum correlation and heteronuclear multi-bond connectivity methods. On similar irradiation for 30 min in degassed aqueous [2% (v/v)] acetonitrile, **3** was formed quantitatively. By contrast, the reaction in degassed aqueous [0.062% (v/v)[12]] benzene for 30 min gave not only **3** but also **7** and **8** in 6%, 23% and 8% yields, respectively, at 60% conversion. In degassed aqueous [0.151% (v/v)[12]] dichloromethane, **3** was formed in 29% yields at 35% conversion with a trace amount of **7**. On irradiation for 20 min under an oxygen atmosphere in dry acetonitrile, **4** was solely formed in 59% yields, at 62% conversion.[1] On the other hand, on irradiation for 60 min under an oxygen atmosphere in dry benzene **4**, **7** and **8** were formed in 3%, 15% and 4% yields, respectively, at 34% conversion. In dry dichloromethane under an oxygen atmosphere, **4** was formed in 37% yield at 55% conversion with a trace amount of **7**. The products are classified into two categories: one consists of **3** and **4**, which favour a polar solvent; and the other pairs **7** and **8**, which prefer a nonpolar solvent. The ratio of yields of **3** or **4** to those of **7** and **8** strongly depends on the solvent. In a series of degassed aqueous solvents, the ratio of 100:0 in acetonitrile changes to >95:<5 in dichloromethane and 16:84 in benzene. Similarly, in a series of dry solvents under an oxygen atmosphere, the ratio of 100:0 in acetonitrile changes to >95:<5 in dichloromethane, and 14:86 in benzene.

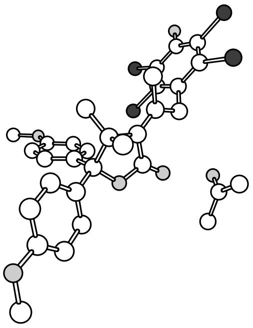


**Figure 1.** The ORTEP drawing of **7** with an acetone molecule. Hydrogen atoms are omitted for clarity.

Scheme 2 shows a plausible reaction mechanism for the CA-sensitised PET reactions of **1** in benzene.[15] Irradiation of CA with **1** gives a contact radical ion pair consisting of $\mathbf{1}^{\cdot+}$ and CA$^{\cdot-}$ ($[\mathbf{1}^{\cdot+}/\mathrm{CA}^{\cdot-}]_{\mathrm{crip}}$) or an exciplex of $\mathbf{1}^{\delta+}$ and CA$^{\delta-}$ ($[\mathbf{1}^{\delta+}/\mathrm{CA}^{\delta-}]_{\mathrm{ex}}$). A quite small portion of $\mathbf{1}^{\cdot+}$ (or $\mathbf{1}^{\delta+}$) converts into $\mathbf{2}^{\cdot+}$ by C-2–C-3 bond cleavage to give **3** and **4** via a similar pathway in acetonitrile.[1] Most of $\mathbf{1}^{\cdot+}$ (or $\mathbf{1}^{\delta+}$) and CA$^{\cdot-}$ (or CA$^{\delta-}$) react within a contact radical ion pair (or an exciplex) to give **7** and **8**. The C-1–C-2 bond dissociative nucleophilic addition[16]

**Table 1.** Solvent effects on the product distribution in the CA-sensitised PET reactions of **1** at 20 °C[a]

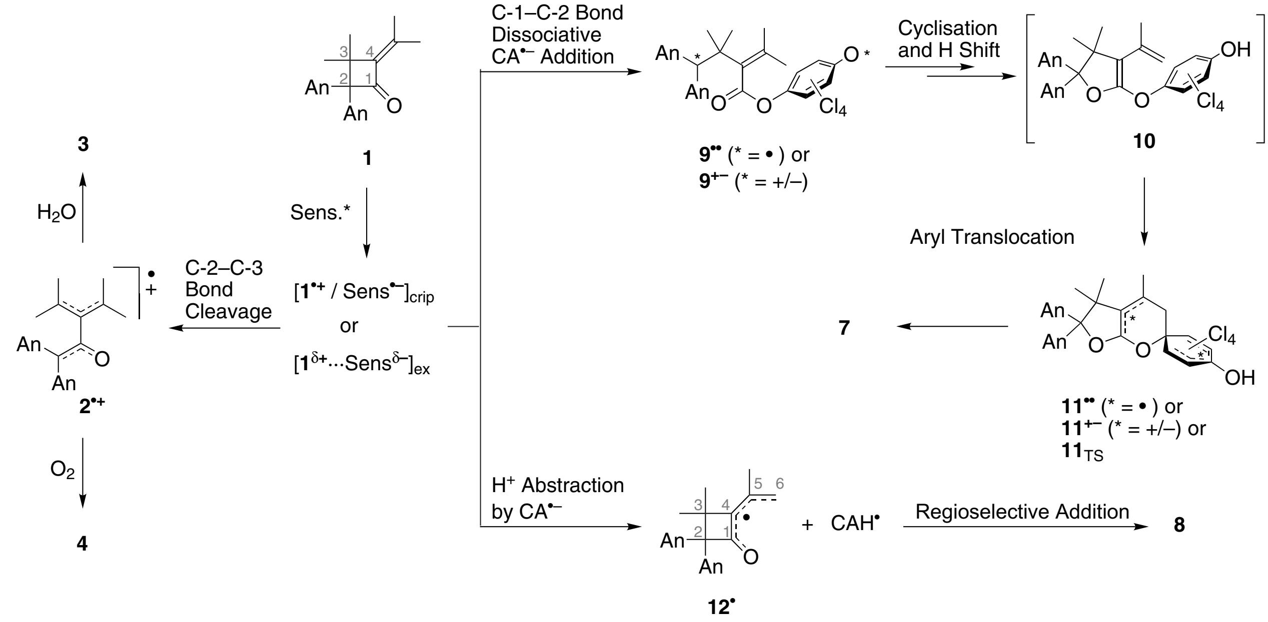
| Atmosphere | Solvents | $H_2O$ % (v/v) | Time (min) | Conv.[b] | Yields[b] | | | | Product ratios (**3** or **4**):(**7** + **8**) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | **3** | **4** | **7** | **8** | |
| Degassed | Acetonitrile[c] | 0 | 30 | 30 | — | — | 0 | 0 | |
| | Dichloromethane | 0 | 30 | 15 | — | — | 4 | 0 | |
| | Benzene | 0 | 60 | 49 | — | — | 27 | 16 | |
| Degassed | Acetonitrile | 2 | 30 | 56 | 56 | — | 0 | 0 | 100:0 |
| | Dichloromethane | 0.151[d] | 30 | 35 | 29 | — | <2 | 0 | >95:<5 |
| | Benzene | 0.062[d] | 30 | 60 | 6 | — | 23 | 8 | 16:84 |
| Oxygen | Acetonitrile[c] | 0 | 20 | 62 | — | 59 | 0 | 0 | 100:0 |
| | Dichloromethane | 0 | 40 | 55 | — | 37 | <2 | 0 | >95:<5 |
| | Benzene | 0 | 60 | 34 | — | 3 | 15 | 4 | 14:86 |

[a] [**1**] = [CA] = 0.01 M.

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

[c] See Ref. 1.

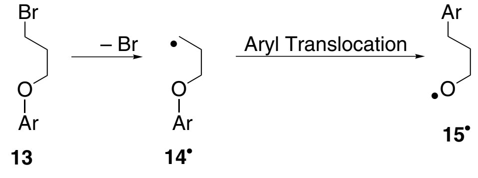
[d] The concentration of water in dichloromethane and benzene saturated with water was 0.151 and 0.062% (v/v), respectively. See Ref. 12.



**Scheme 2.** A plausible mechanism for the CA-sensitised PET reaction of **1** in benzene.

of CA$^{\bullet-}$ to the carbonyl carbon of $\mathbf{1}^{\bullet+}$ gives $\mathbf{9}^{\bullet\bullet}$ or $\mathbf{9}^{+-}$. Cyclisation constructing a dihydrofuran ring and a hydrogen shift probably forms ketal **10**. Finally, a facile rearrangement of the 2,3,5,6-tetrachloro-4-hydroxyphenyl group in **10** occurs to give **7** via a spiro-type intermediate, $\mathbf{11}^{\bullet\bullet}$ or $\mathbf{11}^{+-}$, or the corresponding transition state, $\mathbf{11}_{\text{TS}}$. A similar aryl translocation from an oxygen atom to a carbon atom in an intramolecular *ipso*-substitution mechanism was reported for $\mathbf{14}^{\bullet}$ derived from aryl ether **13** (Scheme 3).[18] In competition with the nucleophilic addition of CA$^{\bullet-}$ to $\mathbf{1}^{\bullet+}$ (or CA$^{\delta-}$ to $\mathbf{1}^{\delta+}$), a proton is abstracted from the isopropylidene subunit of $\mathbf{1}^{\bullet+}$ by CA$^{\bullet-}$ (or $\mathbf{1}^{\delta+}$ by CA$^{\delta-}$) to generate a radical $\mathbf{12}^{\bullet}$ and CAH$^{\bullet}$. CA-adduct **8** is formed by regioselective radical coupling of the C-4 atom of $\mathbf{12}^{\bullet}$ and the oxygen atom in CAH$^{\bullet}$. The regioselectivity is attributed to relaxation of the strain in the methylenecyclobutanone framework, namely the transmutation of the hybrid orbital on the C-4 atom from sp$^3$ into sp$^2$, in the process of the formation of **8** from $\mathbf{12}^{\bullet}$.

In conclusion, we found unusual additions of CA to **1** and observed significant solvent and sensitiser effects on the product distribution. The formation of **7** and **8** can be rationalised by stepwise mechanisms involving an aryl translocation and a regioselective CA addition, respectively. We previously reported that the PET reactions of **5** and **6** strongly depended on the solvents and sensitisers.[7,8] Considering the results presented here, this is also the case with the PET reaction of **1**.



**Scheme 3.** Aryl translocation in $\mathbf{14}^{\bullet}$ in an intramolecular *ipso*-substitution mechanism. Ar = 2-MeO-4-CHOC$_6$H$_3$. See Ref. 18.

## Acknowledgements

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13. The procedure used to isolate **7** and **8** was as follows: A benzene solution (33 mL) containing **1** (231 mg, 0.66 mmol) and CA (391 mg, 1.32 mmol) in a large cylindrical quartz cell (diameter 2.0 cm) was irradiated through a cutoff filter ($\lambda > 440$ nm) using a 2 kW Xe lamp at 20 ± 1 °C under an argon atmosphere for 3 h. After evaporation in vacuo, GPC gave two fractions. Recrystallisation of one gave 93.3 mg (0.16 mmol, 24% yield) of **7** from acetone, and the other gave 92.7 mg (0.16 mmol, 24% yield) of **8** from cyclohexane. Satisfactory elemental microanalyses were obtained for **7** and **8**. Selected data for **7** and **8** are as follows: **7** (containing 3% (mol/mol) acetone from $^1$H NMR analysis): mp 221.5–222.0 °C (colourless cubes from acetone); IR (KBr) 3402, 2980, 1732 cm$^{-1}$; HRMS (ESI) calcd for $C_{29}H_{26}O_5Cl_4Na$ [M+Na$^+$] (three major peaks) 617.0427, 619.0397, 621.0368. Obsd. 617.0429, 619.0397, 621.0365; $^1$H NMR (600 MHz, $CDCl_3$): $\delta_{\mathrm{ppm}}$ 1.25 (s, 6H), 1.72 (s, 3H), 3.82 (s, 6H), 4.77 (s, 2H), 6.22 (br s, 1H), 6.86 (AA′BB′, $J = 9.0$ Hz, 4H), 7.39 (AA′BB′, $J = 9.0$ Hz, 4H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta_{\mathrm{ppm}}$ 17.84, 26.52 (2 C), 37.86, 49.20, 55.25 (2C), 91.51, 113.15 (4C), 119.35 (2C), 128.77 (4C), 129.69 (2C), 132.74 (2C), 133.12, 133.15, 147.51, 148.30, 158.93 (2C), 169.73. Compound **8**: mp 175.5–176.5 °C (colourless plates from cyclohexane); IR (KBr) 3348, 2931, 1736 cm$^{-1}$; HRMS (ESI) calcd for $C_{29}H_{26}O_5Cl_4Na$ [M+Na$^+$] 617.0427, 619.0397, 621.0368. Obsd. 617.0429, 619.0401, 621.0366; $^1$H NMR (600 MHz, $CDCl_3$): $\delta_{\mathrm{ppm}}$ 1.60 (s, 3H), 1.62 (s, 3H), 2.14 (d, $J = 0.8$ Hz, 3H), 3.69 (s, 3H), 3.72 (s, 3H), 5.26 (t, $J = 0.8$ Hz, 1H), 5.41 (s, 1H), 6.03 (s, 1H), 6.70 (AA′BB′, $J = 9.0$ Hz, 2H), 6.72 (AA′BB′, $J = 9.0$ Hz, 2H), 7.27 (AA′BB′, $J = 9.0$ Hz, 2H), 7.42 (AA′BB′, $J = 9.0$ Hz, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$): $\delta_{\mathrm{ppm}}$ 23.53, 24.85, 26.16, 34.39, 47.03, 51.12, 55.01, 55.05, 113.05 (2C), 113.24 (2C), 119.08 (2C), 121.80 (2C), 126.95, 131.07 (2C), 131.89 (2C), 134.23, 134.92, 139.16, 139.32, 147.29, 157.40, 157.43, 167.26.
14. Crystallographic data of **7** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 241920. These data can be obtained free of charge via http://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.
15. The absence of reactivity of **1** under the TCA-sensitised PET conditions in benzene may be attributed to the fast decay of $[\mathbf{1}^{\cdot+}/\mathrm{TCA}^{\cdot-}]_{\mathrm{crip}}$ or $[\mathbf{1}^{\delta+}/\mathrm{TCA}^{\delta-}]_{\mathrm{ex}}$ by back electron transfer, because the efficient electron-transfer quenching of $^1$TCA* by **1** in benzene was confirmed by the large Stern–Volmer constant, $k_q\tau = 145$ M$^{-1}$.
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