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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]dihydrofu-ran-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. © 2005 Elsevier Ltd. All rights reserved.

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<sup>++</sup>, Chart 1) intermediate.<sup>1</sup> Photoinduced electron-transfer (PET) reactions of 2,2-dianisyl-4-isopropylidene-3,3-dimethylcyclobutanone [1, anodic peak potential

 $(E_{ap}^{ox}) = +1.43$  V versus SCE, in acetonitrile] using *p*-chloranil (CA,  $E_{1/2}^{red} = \pm 0.00$  V) or 1,2,9,10-tetracyanoanthracene (TCA, -0.43 V)<sup>2</sup> generated an OTME<sup>+</sup>type intermediate **2**<sup>+</sup>, which was captured by water<sup>3</sup> or molecular oxygen<sup>5</sup> in acetonitrile to give 2,2-dianisyl-4isopropylidene-5,5-dimethyldihydrofuran-3-one (**3**) and



**Chart 1.** The parent OTME<sup> $\cdot+$ </sup>, 2-methylenecyclobutanone derivatives and sensitisers. An = 4-MeOC<sub>6</sub>H<sub>4</sub>.



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

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4,4'-dimethoxybenzophenone (4, Scheme 1).<sup>1</sup> Interestingly, similar PET reactions of the 2-methylenecyclobutanone derivatives, 5 and 6, strongly depend on the solvents and sensitisers.<sup>7–9</sup> A CA-sensitised PET rearrangement from 5 to 6 via the corresponding OTME<sup>++</sup>-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 1<sup>++</sup>, 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.<sup>10</sup>

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).<sup>1</sup> 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)methylethylideneldihydrofuran-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.<sup>13</sup> 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.<sup>14</sup> The structure of  $\mathbf{8}$  was confirmed by spectroscopic analyses,<sup>13</sup> especially <sup>1</sup>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 acetoni-



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

trile, 4 was solely formed in 59% yields, at 62% conversion.<sup>1</sup> 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.

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

Atmosphere	Solvents	H <sub>2</sub> O % (v/v)	Time (min)	Conv. <sup>b</sup>	Yields <sup>b</sup>				Product ratios (3 or 4):(7 + 8)
					3	4	7	8	
Degassed	Acetonitrile <sup>c</sup>	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 <sup>d</sup>	30	35	29		<2	0	>95:<5
	Benzene	0.062 <sup>d</sup>	30	60	6	—	23	8	16:84
Oxygen	Acetonitrile <sup>c</sup>	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

Table 1. Solvent effects on the product distribution in the CA-sensitised PET reactions of 1 at  $20 \,^{\circ}\text{C}^a$ 

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

<sup>b</sup> The conversions and yields were determined by <sup>1</sup>H NMR analysis and are given in %.

<sup>c</sup> See Ref. 1.

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

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