

## Rearrangement of a 2-Methylenecyclobutanone Derivative Triggered by Photoinduced Electron Transfer: An Unprecedented Oxa Analogue of the Tetramethyleneethane Radical Cation

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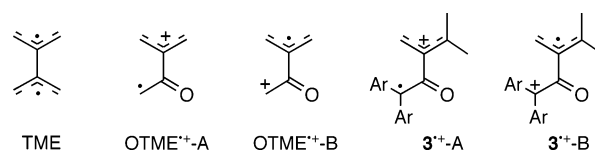
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In a non-Kekulé molecule system, replacing a carbon atom with an oxygen atom induces considerable changes in the geometry, multiplicity, electronic structure, and chemical reactivity of molecules, as exemplified by an oxyallyl,<sup>1</sup> oxa analogue of trimethylenemethane. The oxatetramethyleneethane (3-methylenebutan-2-one-1,4-diyl) radical cation (OTME<sup>•+</sup>) shown in Chart 1 is a radical cation variant of an unprecedented oxa analogue of tetramethyleneethane (TME).<sup>2</sup> Expecting to generate OTME<sup>•+</sup> intermediate 3<sup>•+</sup>, in this work, we studied photoinduced electron-transfer (PET) reactions of 2,2-bis(*p*-methoxyphenyl)-3,3-dimethyl-4-methylenecyclobutanone<sup>3</sup> (**1**, Scheme 1, Ar = 4-MeOC<sub>6</sub>H<sub>4</sub>) and 2,2-bis(*p*-methoxyphenyl)-4-isopropylidencyclobutanone (**2**). We now report a novel rearrangement of **1** to **2** via 3<sup>•+</sup> together with ESR observations of 3<sup>•+</sup>.

On irradiating (2 kW Xe lamp,  $\lambda > 440$  nm) *p*-chloranil (CA,  $E_{\text{cp}}^{\text{red}} = +0.12$  V vs SCE in dichloromethane) for 10 min in degassed benzene, **1** ( $E_{\text{ap}}^{\text{ox}} = +1.61$  V) produced a mixture of **2** and an adduct of CA (**4**) in 5 and 23% yields, respectively, at 39% conversion, as shown in Table 1. Prolonged irradiation for 30 min resulted in the formation of **2** and **4** in 4 and 37% yields, respectively, at 60% conversion. These findings suggest that **4** is formed secondarily from **2** under the conditions used. Actually, similar photoreaction of **2** ( $E_{\text{ap}}^{\text{ox}} = +1.40$  V) with CA gave **4** in benzene in quantitative yield. Interestingly, the reaction of **1** depended strongly on the solvent polarity. Similar PET reactions of **1** to give **2** took place in less polar dichloromethane, albeit in low yield, but not at all in polar acetonitrile, whereas **4** was formed from **2** quantitatively independent of solvent polarity.

A plausible reaction mechanism for CA-sensitized PET reactions of **1** and **2** is shown in Scheme 2. The 1<sup>•+</sup> formed initially undergoes C<sub>2</sub>–C<sub>3</sub> cleavage to give an OTME<sup>•+</sup> intermediate, 3<sup>•+</sup>, which undergoes successive back electron transfer (BET) from CA<sup>•-</sup> to give a neutral OTME-type intermediate, 3.<sup>4</sup> Sequential cyclization finally gives the rearranged product **2**.<sup>5</sup> An alternative pathway from 3<sup>•+</sup> to **2** involves the sequence of cyclization and BET via 2<sup>•+</sup>. The former is thought to be preferable<sup>6</sup> over the latter for 3<sup>•+</sup> because the observed solvent effects imply that the reaction occurs via an exciplex or a contact radical ion pair rather than via a solvent-separated radical ion pair or a free radical ion. Adduct **4** is formed via CA<sup>•-</sup> and the 1,4-radical cation 5<sup>•+</sup> with the 1,1-diarylethyl radical and 3-methylcrotonoyl cation subunits, which is formed from 2<sup>•+</sup> by C<sub>1</sub>–C<sub>2</sub> cleavage after reoxidation of **2**. The difference in the regioselectivity of the bond cleavage between 1<sup>•+</sup> and 2<sup>•+</sup> is an intriguing feature. The C<sub>1</sub>–C<sub>2</sub> cleavage of 2<sup>•+</sup> can be compared to a radical-cation Norrish type I cleavage, as Akaba et al. reported for aralkyl ketones.<sup>7</sup> The driving force of the C<sub>2</sub>–C<sub>3</sub> cleavage of

Chart 1



Scheme 1. CA-Sensitized PET Reactions of **1** and **2**

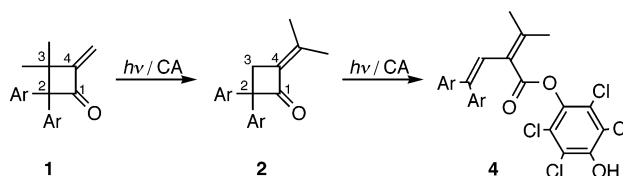
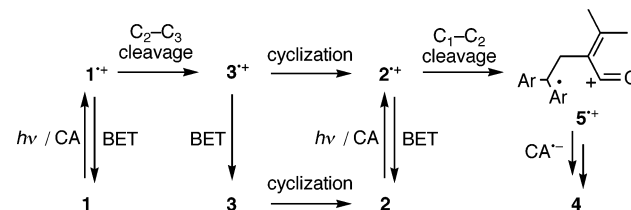


Table 1. CA-Sensitized PET Reactions of **1** and **2**<sup>a</sup>

substrates	solvents	time/min	yields <sup>b</sup>		
			1	2	4
<b>1</b>	benzene	10	61	5	23
		30	40	4	37
	dichloromethane	10	92	8	0
		30	56	7	7
	acetonitrile	10	88	0	0
		30	63	0	0
<b>2</b>	benzene	10	0	41	59
	dichloromethane	10	0	74	24
	acetonitrile	10	0	78	22

<sup>a</sup> [1] = [2] = [CA] = 0.01 M. A small amount of tetrachlorohydroquinone was also formed during the reactions. <sup>b</sup> The yields were determined by <sup>1</sup>H NMR analysis and are given in %.

Scheme 2. A Plausible Reaction Mechanism



1<sup>•+</sup> may be the relaxation of the steric hindrance between the two aryl and methyl groups in the eclipsed conformation of 1<sup>•+</sup>.

Two electronic structures are formally possible for OTME<sup>•+</sup> derivatives (Chart 1). In the case of the parent OTME<sup>•+</sup>, one is type A with the formal ketomethyl radical and allyl cation subunits. Type B, the counterpart of type A, is the other and possesses the ketomethyl cation and allyl radical subunits. According to B3LYP/Aug-cc-pVTZ and MP2/cc-pVTZ calculations,<sup>8</sup> the parent OTME<sup>•+</sup> prefers a slightly twisted structure for type A with dihedral angles of  $\theta = \sim 27^\circ$  and  $\omega = \sim -2^\circ$  (Figure 1a, Table 2). The sum of the

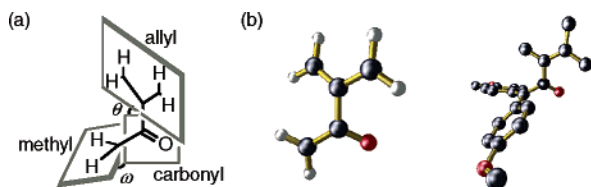
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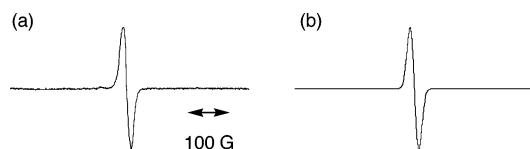
**Table 2.** Calculated Dihedral Angles ( $\theta$  and  $\omega$ ), the Sum of the Partial Spin and Charge Densities ( $\Sigma\rho$  and  $\Sigma q$ ), and Types of Electronic Structures<sup>a</sup>

radical cation	methods	$\theta$ /deg	$\omega$ /deg	$\Sigma\rho$			$\Sigma q$			types
				allyl	carbonyl	methyl	allyl	carbonyl	methyl	
OTME <sup>•+</sup>	B3LYP/Aug-cc-pVTZ	+27.2	-1.0	-0.02	+0.32	+0.71	+0.89	+0.21	-0.11	A
	MP2/cc-pVTZ	+27.0	-3.3	0.00	+0.11	+0.89	+0.84	+0.05	+0.11	A
3 <sup>•+</sup>	AM1/UHF	+25.4	+90.6	+0.01	-0.06	+1.05	+0.85	+0.08	+0.07	A
	B3LYP/cc-pVDZ	+9.2	+90.1	+1.03	-0.03	0.00	+0.22	-0.12	+0.90	B
	B3LYP/6-31G(d,p)	+10.9	+88.4	+1.03	-0.03	0.00	+0.23	-0.12	+0.89	B

<sup>a</sup> All calculations were carried out using unrestricted open-shell wave functions.



**Figure 1.** (a) Definition of the dihedral angles ( $\theta$  and  $\omega$ ) and three subunits in the OTME framework. (b) The optimized geometry of the parent OTME<sup>•+</sup> and 3<sup>•+</sup> (hydrogen atoms are omitted for clarity) using B3LYP/Aug-cc-pVTZ and AM1/UHF, respectively.



**Figure 2.** (a) ESR spectrum observed after  $\gamma$ -ray irradiation of **1** in *n*-BuCl glassy matrix at 77 K. (b) Simulation spectrum for 3<sup>•+</sup>.

calculated partial spin density ( $\Sigma\rho$ ) of the methyl subunit of the parent OTME<sup>•+</sup> is markedly higher than those of the allyl and carbonyl parts. Accordingly, the sum of the calculated partial charge density ( $\Sigma q$ ) of the allyl part is higher than the values for the carbonyl and methyl parts. Interestingly, however, the electronic structure of 3<sup>•+</sup> changes depending on the calculation method. Unlike the B3LYP calculation for the parent OTME<sup>•+</sup>, the B3LYP calculations for 3<sup>•+</sup> suggest that it is type B with  $\theta = \sim 10^\circ$ , whereas the AM1/UHF calculation still holds that 3<sup>•+</sup> is type A with  $\theta = 25.4^\circ$ .

The appropriate electronic structure of 3<sup>•+</sup> is given by the CW ESR spectrum observed after  $\gamma$ -ray irradiation of **1** in *n*-BuCl glassy matrix at 77 K (Figure 2a).<sup>9</sup> A simple spectrum with  $g = 2.0027$  is tentatively assigned to 3<sup>•+</sup> in comparison with the simulated spectrum with a hyperfine coupling constant,  $\alpha_{\text{H}} = 3.5$  (4  $H_{\text{O}}$ ) and 1.5 G (4  $H_{\text{m}}$ ) for 3<sup>•+</sup> (Figure 2b). The spectrum is obviously different from the observed and simulated spectra<sup>10</sup> with  $\alpha_{\text{H}}$  reported for the 1,1-dimethylallyl radical,<sup>11</sup> a subunit of 3<sup>•+</sup> in type B. Consequently, these findings indicate that if 3<sup>•+</sup> is really generated under the conditions used, the appropriate electronic structure of 3<sup>•+</sup> is type A, contrary to the result of the B3LYP calculations. This may be due to overestimation for the contribution of delocalization of an unpaired electron. The  $g$  and  $\alpha_{\text{H}}$  values of 3<sup>•+</sup> are comparable to those [ $g = 2.0026$ ,  $\alpha_{\text{H}} = 3.18$  (4  $H_{\text{O}}$ ) and 1.26 G (4  $H_{\text{m}}$ )] of the structurally related 1,1-diphenylpropan-1-yl radical,<sup>12</sup> while the  $g$  value of 3<sup>•+</sup> is smaller than that ( $g = 2.0040$ ) of the 3-methylbutan-2-on-3-yl radical,<sup>13</sup> which can take a planar structure. These findings suggest that the diarylmethyl subunit in 3<sup>•+</sup> is so twisted that it does not interact electronically with the carbonyl subunit. This is not inconsistent with the AM1/UHF calculation for 3<sup>•+</sup>, in which the  $\Sigma\rho$  value of the diarylmethyl subunit is almost unity and the diarylmethyl radical and the carbonyl subunits are both twisted with respect to each other, as shown in Figure 1b. The large deviation from the planar structure is probably

due to the radical stabilizing effects of the two aryl groups and steric hindrance between the aryl and allyl groups in 3<sup>•+</sup> with a hypothetical planar structure.

In conclusion, we found a novel rearrangement of **1** via an unprecedented OTME<sup>•+</sup> derivative, 3<sup>•+</sup>, which was successfully detected by ESR in a low-temperature glassy matrix. This work produced a new substance in the field of non-Kekulé chemistry, which will affect related fields of reactive intermediate, electron-transfer chemistry, and organic photochemistry. Further studies of the mechanism are now in progress and will be published elsewhere.

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**Supporting Information Available:** Physical data on **1**, **2**, and **4**, experimental details of the photoreaction, and material concerning refs 4, 6, 8, and 10 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (5) A similar BET-cyclization sequence has been reported recently. See: Ikeda, H.; Akiyama, K.; Takahashi, Y.; Nakamura, T.; Ishizaki, S.; Shiratori, Y.; Ohaku, H.; Goodman, J. L.; Houmam, A.; Wayner, D. D. M.; Tero-Kubota, S.; Miyashii, T. *J. Am. Chem. Soc.* **2003**, *125*, 9147–9157.
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- (8) Details of the calculation are given in the Supporting Information.
- (9) The same matrix exhibited an absorption spectra with maximum at 348 nm, also suggesting the formation of 3<sup>•+</sup> in type A because the absorption corresponds to an absorption of bis(*p*-4-methoxyphenyl)methyl radical (350 nm in dichloromethane). See ref 5.
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