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# Photoinduced Electron Transfer Ring Opening of α-Epoxyketones Using 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ)

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Photoinduced electron transfer ring opening of  $\alpha$ -epoxyketones using 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) in methanol and acetic acid solutions resulted in the formation of diastereomeric products, hydroxy ethers and hydroxy esters, respectively. However, the formation of *cis*-1,3-dioxolanes and *cis*-spirodioxolanes has been observed on reaction in acetone and cyclohexanone solutions, respectively. The effect of the electron donating character of the substituent influenced the rate of the ring opening. Quantum computational studies explain the mechanism of the addition.

Keywords: α-Epoxyketones, Ring opening, Photochemistry, Photo-electron transfer

## **INTRODUCTION**

Single electron transfer (SET)-induced ring opening of epoxides and  $\alpha$ -epoxyketones is of great interest not only in thermal reactions but also in photochemical reactions. The ring opening of these compounds in the presence of various nucleophiles leads to the formation of some interesting compounds such as ethers, dioxolanes, and trioxolanes. Various catalysts or photocatalysts such as ceric ammonium nitrate (CAN) [1,2], 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) [3], iron(III) chloride [4], 9,10-dicyanoanthracene (DCA) [5], tetracyanoethylene (TCNE) [6], and 2,4,6triphenylpyrylium tetrafluoroborate (TPT) [7] have so far been used for this purpose. 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) has been used as an electron acceptor in many photoinduced electron transfer reactions [8-13].

Recently, we have reported on the photocatalytic ring opening of certain  $\alpha$ -epoxyketones **1a-1g** by 2,4,6-triphenylpyrylium tetrafluoroborate **2** (TPT) as a photocatalyst

in methanol [14], acetic acid [15], acetone [16], and cyclohexanone [17] solutions. As a continuation of our studies with  $\alpha$ -epoxyketones, we have investigated their electron-donor ability toward photoexcited TCNQ (12) in methanol, acetic acid, acetone, and cyclohexanone solutions to elucidate the effect of the electron acceptor (photocatalyst) on the rate of the ring opening and on the diastereoselectivity of the reaction.

## EXPERIMENTAL

All photoproducts are known and their spectroscopic data have been already reported [14-17]. <sup>1</sup>H NMR spectra were measured in CDCl<sub>3</sub> solutions containing TMS as an internal standard on Bruker AW 80 (80 MHz) and Bruker DRX-500 (500 MHz) spectrometers. Preparative layer chromatography (PLC) was carried out on  $20 \times 20$  cm<sup>2</sup> plates coated with a 1 mm layer of Merck silica gel PF<sub>254</sub>, which was applied as a slurry and air dried. All irradiations were carried out using a 400 W, high pressure, Hg vapor lamp from Narva, and samples were cooled in Duran glass using running cold water. The light was passed through a filter solution (76 g dm<sup>-3</sup> of

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Scheme 1

NaNO<sub>2</sub> and 4.4 g dm<sup>-3</sup> of CuSO<sub>4</sub> in 2.7 M NH<sub>4</sub>OH) to obtain  $\lambda \ge 400$  nm for the selective excitation of **2** and **12** to prevent to absorption of light by **1a-1g**.

A solution of **1a-1g** and photocatalysts **2** or **12** in methanol (Table 1), acetic acid (Table 2), acetone (Table 3), and cyclohexanone (Table 4) was irradiated for the amount of time

given in Tables 1-4, using the molar ratios mentioned in the footnotes of each table.

## **RESULTS AND DISCUSSION**

Irradiation ( $\lambda \ge 400$  nm) of each of the  $\alpha$ -epoxyketones **1a**-

|  | ТРТ            |                |        |         |                         |  |                |            | TCNQ   |         |                    |
|--|----------------|----------------|--------|---------|-------------------------|--|----------------|------------|--------|---------|--------------------|
| Concn.<br>of <b>1a-1f</b> <sup>a</sup> | Irrad.<br>time | Yield          | Produc | ets (%) | Ratio                   | Concn.<br>of <b>1a-1f</b> <sup>a</sup> | Irrad.<br>time | Yield      | Produc | ets (%) | Ratio <sup>d</sup> |
| (mM)                                   | $(h)^{b}$      | $(\%)^{\rm c}$ | 3      | 4       | <b>3:4</b> <sup>d</sup> | (mM)                                   | $(h)^{b}$      | $(\%)^{c}$ | 3      | 4       | 3:4                |
| <b>a</b> (56)                          | 8              | 53 (96)        | 29     | 71      | 1:2.4                   | <b>a</b> (50)                          | 13             | 62 (97)    | 32     | 68      | 1:2.1              |
| <b>b</b> (52)                          | 6              | 71 (91)        | 46     | 54      | 1:1.2                   | <b>b</b> (50)                          | 8              | 81 (97)    | 50     | 50      | 1:1                |
| <b>c</b> (52)                          | 7              | 60 (88)        | 14     | 86      | 1:6.2                   | <b>c</b> (50)                          | 13             | 60 (95)    | 25     | 75      | 1:3                |
| <b>d</b> (49)                          | 5              | 93 (93)        | 52     | 48      | 1.1:1                   | <b>d</b> (50)                          | 8              | 88 (95)    | 50     | 50      | 1:1                |
| <b>e</b> (49)                          | 7              | 62 (92)        | 25     | 75      | 1:3                     | <b>e</b> (50)                          | 13             | 62 (93)    | 20     | 80      | 1:4.1              |
| <b>f</b> (40)                          | 3              | 99 (99)        | 50     | 50      | 1:1                     | <b>f</b> (50)                          | 8              | 74 (81)    | 50     | 50      | 1:1                |

Table 1. Photocatalytic Ring Opening of 1a-1f in Methanol Solution by TPT [14] (2) and TCNQ (12)

<sup>a</sup>[2] = 3.15 mM. <sup>b</sup>Times are given after total disappearance of **1a-1f**. <sup>c</sup>Based on the amount of **1a-1f** used (consumed). <sup>d</sup>The ratios have been determined by comparison of the integral ratios of the methoxy groups at C-3 in the <sup>1</sup>H NMR spectra of the isolated mixture of products. <sup>e</sup>[**12**] = 1.25 mM.

1g in the presence of either TPT (2) or TCNQ (12) as photocatalysts in methanol, acetic acid, acetone or cyclohexanone solutions resulted in the opening of the epoxide ring and formation of solvent-cooperated products 3-8 and 11; also products 9 and 10 were obtained upon cleavage of the epoxide ring C-C bonds (Scheme 1). It should be noted that no reaction has been observed in the absence of photocatalyst 2 or 12. A comparison of the UV-spectra of 2 and 12 with those of 1a-1g indicated that 1a-1g do not exhibit effective absorbance above 350 nm. This means that excitation of  $\alpha$ -epoxyketones 1a-1g is not possible under our experimental conditions ( $\lambda \ge$ 400 nm).

As shown in Tables 1-4, the formation of the same products has been observed upon irradiation of all  $\alpha$ epoxyketones investigated here in the presence of both photocatalysts, except for the photoreaction of **1a-1f** in acetone solution using TCNQ as a photocatalyst, in which only the formation of *cis*-dioxolane **8a-8f**, in addition to the alcoholic products **9a**, **9b**, and **10**, was observed (see Table 3). We have previously proposed the mechanism of the ring opening of **1a-1f** in the presence of TPT in methanol solution [8]. These results indicated that the diastereomeric ratios of products **3a-3f:4a-4f** are dependent on the involvement of intermediates **13-15** (in which their stability and responsibility in the reaction are directly related to the nature of the substituents, especially for those that are on the phenyl ring



Scheme 2

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|                       |                                 | TPT                               |                                  |                       | TCNQ                            |   |                           |  |
|-----------------------|---------------------------------|-----------------------------------|----------------------------------|-----------------------|---------------------------------|---|---------------------------|--|
| <b>1</b> <sup>a</sup> | Irrad. time<br>(h) <sup>b</sup> | Products (yield%)<br><b>5 + 6</b> | ratio <sup>c</sup><br><b>5:6</b> | <b>1</b> <sup>d</sup> | Irrad. time<br>(h) <sup>e</sup> | Products (yield%) <sup>f</sup><br>5 + 6 | ratio <sup>c</sup><br>5:6 |  |
| a                     | 6                               | 54                                | 1:1.3                            | a                     | 18                              | 59 (95)                                 | 1:1.27                    |  |
| b                     | 3                               | 69                                | 1:1.4                            | b                     | 12                              | 79 (97)                                 | 1:1.41                    |  |
| c                     | 6                               | 54                                | 1:1.8                            | с                     | 18                              | 60 (96)                                 | 1:1.15                    |  |
| d                     | 2                               | 71                                | 1:1.1                            | d                     | 10                              | 83 (98)                                 | 1:1.24                    |  |
| e                     | 6                               | 59                                | 1.6:1                            | e                     | 18                              | 66 (95)                                 | 1.22:1                    |  |
| g                     | 15                              | 53                                | 1.1:1                            | g                     | 32                              | 57 (95)                                 | 1.4:1                     |  |

Table 2. Photocatalytic Ring Opening of 1a-1e and 1g in Acetic Acid Solution by TPT [15] (2) and TCNQ (12)

<sup>a</sup>[**1a-1e** and **1g**] = 40 mM and [**2**] = 4 mM. <sup>b</sup>The times are given after total disappearance of **1a-1e** and **1g**. <sup>c</sup>The ratios have been determined by comparison of the integral ratio of the methyl groups of the acetyl moiety at C-1 in the <sup>1</sup>H NMR spectra of the isolated mixture of products. <sup>d</sup>[**1a-1e** and **1g**] = 50 mM and [**12**] = 1.25 mM. <sup>c</sup>The times are given after maximum progression of the reaction. <sup>f</sup>Based on the amount of **1a-1e** and **1g** used (consumed).

| TPT                   |                       |    |            |              |                | TCNQ                  |         |                           |  |
|-----------------------|-----------------------|----|------------|--------------|----------------|-----------------------|---------|---------------------------|--|
| <b>1</b> <sup>a</sup> | Irrad.                | P  | roducts (y | vield%)      | 1 <sup>c</sup> | Irrad.                | Produc  | cts (yield%) <sup>e</sup> |  |
| _                     | time (h) <sup>b</sup> | 7  | 8          | Alcohol      |                | time (h) <sup>d</sup> | 8       | Alcohol                   |  |
| a                     | 10                    | 14 | 23         | <b>10</b> 30 | a              | 25                    | 25 (41) | <b>10</b> 24 (39)         |  |
| b                     | 4                     | 10 | 28         | 10 28        | b              | 14                    | 35 (60) | <b>10</b> 17 (28)         |  |
| c                     | 9                     | 11 | 24         | <b>9a</b> 41 | c              | 15                    | 24 (35) | <b>9a</b> 30 (44)         |  |
| d                     | 4                     | 11 | 29         | <b>10</b> 21 | d              | 12                    | 32 (54) | <b>10</b> 30 (44)         |  |
| e                     | 10                    | 8  | 27         | <b>9b</b> 42 | e              | 25                    | 26 (38) | <b>9b</b> 33 (48)         |  |
| f                     | 4                     | -  | 23         | <b>9b</b> 38 | f              | 11                    | 25 (42) | <b>9b</b> 17 (28)         |  |

Table 3. Photocatalytic Ring Opening of 1a-1f in Acetone Solution by TPT [16] (2) and TCNQ (12)

<sup>a</sup>[**1a-1f**] = 40 mM and [**2**] = 4 mM. <sup>b</sup>The times are given after total disappearance of starting **1a-1f**. <sup>c</sup>[**1a-1f**] = 50 mM and [**12**] = 1.25 mM. <sup>d</sup>The times are given after maximum progression of the reaction. <sup>e</sup>Based on the amount of **1a-1f** used (consumed).

attached to the epoxide ring) and their stabilizing effect of a cation center (see Table 1 and Scheme 2).

A comparison of the molar extinction coefficients ( $\varepsilon$ ) of both photocatalysts in acetone solution at the wavelength of irradiation, i.e. TPT UV (CH<sub>3</sub>COCH<sub>3</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 407.5 nm (25250) and TCNQ UV (CH<sub>3</sub>COCH<sub>3</sub>):  $\lambda_{max}$  ( $\varepsilon$ ) = 395.5 nm (62550), shows that, under the experimental conditions used in this work, the probability of exciting TCNQ is 2.5 times greater than that of TPT. Therefore, according to the second order kinetics of the reaction, with the same irradiation time one would expect the formation of the complex of  $\alpha$ epoxyketones and TCNQ to be faster than that of  $\alpha$ epoxyketones and TPT. If this were the case, a better conversion of  $\alpha$ -epoxyketones would be obtained under TCNQ catalysis. However, due to the low solubility of TCNQ in acetone, the actual experimental concentration ratio of **1a**-

|                       |                                 | TPT                                  |                       | TCNQ                            |                                      |  |  |
|-----------------------|---------------------------------|--------------------------------------|-----------------------|---------------------------------|--------------------------------------|--|--|
| <b>1</b> <sup>a</sup> | Irrad. time<br>(h) <sup>b</sup> | Products (yield%) <sup>c</sup><br>11 | <b>1</b> <sup>d</sup> | Irrad.<br>time (h) <sup>b</sup> | Products (yield%) <sup>c</sup><br>11 |  |  |
| a                     | 5                               | 27 (34)                              | a                     | 7                               | 54 (90)                              |  |  |
| b                     | 2.5                             | 31 (35)                              | b                     | 4                               | 66 (97)                              |  |  |
| c                     | 5                               | 26 (33)                              | c                     | 7                               | 52 (90)                              |  |  |
| d                     | 2                               | 33 (37)                              | d                     | 3                               | 71 (95)                              |  |  |
| e                     | 5                               | 30 (34)                              | e                     | 7                               | 52 (93)                              |  |  |
| g                     | 15                              | 24 (34)                              | g                     | 22                              | 40 (91)                              |  |  |

Table 4. Photocatalytic Ring Opening of 1a-1e and 1g in Cyclohexanone Solution by TPT [17](2) and TCNQ (12)

<sup>a</sup>[1a-1e and 1g] = 40 mM and [2] = 4 mM. <sup>b</sup>The times are given after maximum progression of the reaction. <sup>c</sup>Based on the amount of 1a-1e and 1g used (consumed). <sup>d</sup>[1a-1e and 1g] = 40 mM, [12] = 2 mM.

**1f**:TCNQ in acetone solution was 40:1, while the concentration ratio of **1a-1f**:TPT in the same solution was 10:1. Therefore, the lower relative concentration is one reason for the longer irradiation time to complete the reaction in the presence of TCNQ.

As a test experiment, we irradiated **1a** and **1d** in the presence of TPT at a molar ratio of 25:1. This showed a total disappearance of **1a** and **1d** after 20 and 9 h, respectively. In contrast, irradiation of the same molar ratios using TCNQ instead of TPT showed that the reactions were still not complete after 25 h for **1a** and 12 h for **1d**. These results indicate that TPT is a more powerful electron acceptor in the excited state than TCNQ.

A more interesting result was that the diastereomeric ratios of products were totally different in the presence of TPT than TCNQ. These observations can be explained theoretically using PM3 quantum mechanical computation.

#### **Computational Studies**

The substituent effect on the preferred involvement of one of the intermediates **13-15** in the reaction and on the behavior of the photocatalyst in the formation of different diastereomeric ratios of products prompted us to carry out a theoretical study using *semi-empirical* PM3 calculations [18,19]. As shown in Table 5, the presence of electron donor groups on the phenyl ring attached to the epoxide ring (in **1b**, **1d** and **1f**) influenced the increase in  $C_{\beta}$ -O bond polarity. Therefore, the electric charge at  $C_{\beta}$  (C-3) is becoming more positive, while the electric charge at the oxygen atom is becoming more negative. On the other hand, the presence of the same substituent on the phenyl ring of the benzoyl group (in **1c** and **1e**) does not have any significant effect on the polarization of the  $C_{\beta}$ -O bond.

The interesting result in these calculations is that the resonance effect of the methoxy group in comparison to the inductive effect of the methyl group resulted in better polarization of the  $C_{\beta}$ -O bond. This explains the preferred involvement of intermediate **15** in the case of the methoxy substituent for the nucleophilic attack, which then leads to the formation of a 1:1 ratio of diastereomeric products. The calculated electric charges are accurate to within three decimal points.

In the study of the geometry of the charge transfer complex between  $\alpha$ -epoxyketones and TPT or TCNQ, a relaxed geometry optimization is used to allow any changes due to intermolecular interaction. Electric charge distribution between the two parts of the complex clearly shows the existence of a charge transfer (CT) complex. The calculated values of the total dipole moment of the molecules show, again, the effect of the donor group on the polarity of the

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|   | El           | ectric charge |         | Total dipole moment |
|---|--------------|---------------|---------|---------------------|
| 1 | $C_{\alpha}$ | $C_{m eta}$   | 0       | (Debye)             |
| a | -0.082       | 0.082         | -0. 229 | 2.852               |
| b | -0.083       | 0.084         | -0.231  | 3.030               |
| c | -0.083       | 0.082         | -0.231  | 3.000               |
| d | -0.084       | 0.089         | -0.233  | 3.153               |
| e | -0.083       | 0.082         | -0.232  | 3.731               |
| f | -0.083       | 0.088         | -0. 234 | 3.035               |
| g | -0.083       | 0.085         | -0.229  | 2.465               |

 Table 5.
 Mulliken Electric Charges [21,22] of Epoxide Ring Atoms of Neutral α-Epoxyketones 1a-1g and Their Total Dipole Moments by Quantum Mechanical PM3 Calculation.





compounds.

Results of the PM3 calculations on the charge transfer complexes of **1a-1g** with TPT and TCNQ also indicate that **1a-1g** (structure **16**) form stronger complexes with TPT than with TCNQ (structure **17**) (Scheme 3) shows as an example **16a** for **1a** with TPT and **17a** for **1a** with TCNQ. These structures correspond to the minimum point of the intermolecular interaction potential energy surface approached from several different initial configurations. These optimizations are carried out for the solvent-free gas phase charge transfer complexes on a comparative basis.

The results obtained for the effect of the interaction between  $\alpha$ -epoxyketones and TPT or TCNQ can be applied to the interaction in the presence of solvent, taking into account the electric dipole moment of the isolated species and complexes (Table 6).

A comparison between the electric charges of the epoxide ring atoms shows that the electric charge at C-3 ( $C_{\beta}$ ) (and

| 1 |              | 16a – 1     | 6g (1a – 1 | g + TPT    | )       | 17a – 17g (1a – 1g + TCNQ) |             |        |            |         |
|---|--------------|-------------|------------|------------|---------|----------------------------|-------------|--------|------------|---------|
|   | Elec         | etric char  | ge         | $d(Å)^{a}$ | Total µ | Ele                        | ectric char | ge     | $d(Å)^{a}$ | Total µ |
|   | $C_{\alpha}$ | $C_{\beta}$ | 0          |            | (Debye) | $C_{\alpha}$               | $C_{\beta}$ | 0      |            | (Debye) |
| a | -0.075       | 0.095       | -0.274     | 3.806      | 9.614   | -0.080                     | 0.088       | -0.248 | 3.751      | 3.587   |
| b | -0.077       | 0.098       | -0.275     | 3.878      | 10.071  | -0.080                     | 0.089       | -0.251 | 3.853      | 3.288   |
| c | -0.076       | 0.095       | -0.274     | 3.904      | 10.180  | -0.082                     | 0.085       | -0.249 | 3.799      | 3.409   |
| d | -0.077       | 0.098       | -0.275     | 3.966      | 11.998  | -0.080                     | 0.092       | -0.253 | 3.854      | 3.482   |
| e | -0.078       | 0.093       | -0.275     | 3.921      | 10.894  | -0.083                     | 0.084       | -0.247 | 3.827      | 3.867   |
| f | -0.073       | 0.097       | -0.275     | 4.056      | 12.886  | -0.080                     | 0.093       | -0.253 | 4.031      | 3.413   |
| g | -0.075       | 0.095       | -0.274     | 3.805      | 13.147  | -0.081                     | 0.091       | -0.247 | 3.453      | 2.942   |

**Table 6.** Mulliken Electric Charges [21,22] of Epoxide Ring Atoms and Total Dipole Moment of Complexesof **1a-1g** with TPT (Structure **16**) and with TCNQ (Structure **17**) by PM3 Calculation

<sup>a</sup>d is the intermolecular distance between the photocatalyst and reactant in the optimized equilibrium geometry of the charge transfer complex defined in Scheme 3.





oxygen) in complexes **16a-16g** is more positive (and more negative) than those in complexes **17a-17g**. These results are also supported by the increased total dipole moment of **1a-1g** in the presence of TPT over that in the presence of TCNQ. The intermolecular distances, d, between the photocatalysts and reactants in the equilibrium geometry of the charge transfer complexes have also been listed in Table 6. This signifies the higher electron withdrawing character of TPT. These data are in agreement with the experimental data in that

they predict shorter irradiation times in all reactions using TPT as a photocatalyst.

The validity of the present *semi-empirical* PM3 calculations was tested by substituting an oxygen atom in the epoxide ring with a sulfur atom (Scheme 4

shows the structure **18a** in the case of **1a** after substitution of oxygen by sulfur).

A comparison of the data obtained for the two sets of compounds with oxygen (Table 6) and sulfur atoms (Table 7)

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| 18 | Unoptimiz | ed structure <sup>a</sup> | Optimized structure |           |  |  |
|----|-----------|---------------------------|---------------------|-----------|--|--|
|    | d (Å)     | μ (Debye)                 | d (Å)               | μ (Debye) |  |  |
| a  | 3.496     | 9.239                     | 4.014               | 10.664    |  |  |
| b  | 3.505     | 9.348                     | 4.045               | 10.752    |  |  |
| c  | 3.536     | 9.964                     | 4.083               | 11.253    |  |  |
| d  | 3.542     | 10.939                    | 4.109               | 12.495    |  |  |
| e  | 3.556     | 10.361                    | 4.055               | 11.866    |  |  |
| f  | 3.624     | 11.895                    | 4.100               | 13.231    |  |  |
| g  | 3.458     | 12.302                    | 3.961               | 13.820    |  |  |

 Table 7. Total Dipole Moment and Intermolecular Distance in the Sulphur Containing Complexes 18a-18g by PM3 Calculation

<sup>a</sup>Unoptimized initial structures were based on the optimized structures of the corresponding oxygen-containing compounds.





shows the success of these calculations in distinguishing between the electric effects of the two atoms on the optimized structures and electronic properties of these compounds, as well as on their interactions with photocatalysts. The data listed in Table 7 further show that the O/S substitution effectively changes the dipole moment and also the intermolecular distances in the charge transfer complexes (Scheme 4). A set of calculations at the CIS (singly-excited configuration interaction) level of theory [20,21] based on PM3 wave functions has been carried out on reactants **1a-1g**, photocatalysts TPT and TCNQ, and their respective charge transfer complexes, **16a-16g** and **17a-17g**, to support the results already obtained in our calculations. The results of these calculations reveal that compounds **1a-1g** do not show any UV absorption above the wavelength of 300 nm, while the

photocatalysts have characteristic absorption at 425.9 and 369.3 nm for TPT, and at 395.5 nm for TCNQ. The formation of charge transfer complexes with these two photocatalysts results in the appearance of new strong absorptions in the range of 340-400 nm (see supplementary materials for the numerical values and relative intensities of the absorption wavelengths).

The most interesting point in this study concerns the reaction of **1a-1f** in acetone solution in the presence of both photocatalysts. As shown in Table 3, while the formation of diastereomeric 1,3-dioxolanes 7a-7e and 8a-8f has been observed in the presence of TPT, only the cis-1,3-dioxolanes 8a-8f have been obtained in the presence of TCNQ. Since the reaction is very slow in the presence of TCNQ, it should be expected that structure 19 is formed after electron transfer to TCNQ. The presence of the TCNQ  $\cdot$  radical anion adjacent to the epoxide ring causes a steric hindrance for the nucleophilic attack of acetone from the upper side. In contrast, in structure **20**, which is formed after electron transfer to TPT, the  $BF_4^$ anion, which is the counter ion of the epoxide radical cation, makes a nucleophilic attack on acetone from both possible sides. Therefore, in contrast to TCNQ, the formation of both cis and trans-dioxolanes should be expected in the presence of TPT (Scheme 5).

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