

# Acid Catalysis vs. Electron-Transfer Catalysis via Organic Cations or Cation-Radicals as the Reactive Intermediate. Are These Distinctive Mechanisms?

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## Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

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Proton transfer to aromatic and olefinic donors (D) leads to the facile interchange of transient carbocations ( $DH^+$ ) and cation-radical ( $D^{\cdot+}$ ). The same types of cation and cation-radical are reactive intermediates in the acid catalysis and the electron-transfer catalysis of such organic transformations as benzylic coupling, epoxide/pinacol rearrangements and *cis-trans* isomerization of stilbenes when they are both carried out under otherwise identical reaction conditions. However, the rapid exchange of diamagnetic cations and paramagnetic cation-radicals blurs the traditional view of separate electrophilic and homolytic processes, and rigorous experimental evidence is required to establish whether acid catalysis and electron-transfer catalysis actually represent distinct mechanistic categories.

Acid catalysis, particularly by Brønsted acids, has been extensively applied to diverse organic reactions, including the enhancement of Diels–Alder and related cycloadditions,<sup>1</sup> Claisen rearrangements,<sup>2</sup> hydrolysis of acetals and ketals,<sup>3</sup> epoxide and pinacol rearrangements,<sup>4,5</sup> additions to enol ethers,<sup>6</sup> olefin isomerizations,<sup>7</sup> aromatic benzylations,<sup>8</sup> benzil and benzidine rearrangements,<sup>9</sup> and a wide variety of other organic transformations.<sup>10,11</sup> In a mechanistic context, *proton transfer* to an organic substrate (D) is tantamount to a two-electron oxidation of D,<sup>12</sup> and the catalytic activation generally derives from the enhanced electrophilic reactivity of the intermediate cationic adduct.

There are increasing numbers of reports of an alternative mode of activation that derives via the one-electron oxidation of the organic substrate by ammonium cations ‘magic blue’, arene cation-radicals, etc.; and the catalytic process has been termed *electron-transfer chain* (ETC) catalysis by Chanon,<sup>13</sup> or equivalently, hole catalysis by Bauld<sup>14</sup> and the  $S_{ON}2$  mechanism by Ebersson.<sup>15,16</sup> Catalytic activation induced by electron-transfer derives from the enhanced homolytic reactivity of the cation-radical intermediate, and it has been reported for Diels–Alder and related cycloadditions,<sup>17</sup> pinacol and epoxide rearrangements,<sup>18,19</sup> olefin oxygenations,<sup>20</sup> Claisen

rearrangements,<sup>21</sup> and Gomberg–Bachmann arylations among others.<sup>22</sup>

Catalysis by proton transfer differs from electron-transfer catalysis in that the reactive intermediates are diamagnetic cations as opposed to paramagnetic cation-radicals; and such a traditional (ionic vs. radical) dichotomy has encouraged organic chemists to keep the two catalytic processes in separate, discrete mechanistic categories. However, proton transfer and electron transfer are intrinsically rapid processes, leading to intermediates (i.e., cations and cation-radicals) that are transient and not readily identified. Moreover, the chemical reactivities of paramagnetic cation-radicals are often similar to those of diamagnetic cations, especially toward nucleophiles and related bases. Furthermore, Hart and coworkers<sup>23</sup> showed that the protonation of an aromatic donor (D) to afford its conjugate acid ( $DH^+$ ) can also lead to the cation-radical ( $D^{\cdot+}$ ). Such an interchange between diamagnetic and paramagnetic intermediates raises the possibility that acid catalysis and electron-transfer catalysis may not be as clearly differentiated as formerly thought.<sup>24,25</sup> In order to address this difficult mechanistic problem, we present our preliminary investigation in two separate, inter-related parts. In **Part 1**, we re-examine the oxidative conversion of Hart’s octamethylbiphenylene (OMB) donor by Brønsted acids, and then develop useful procedures for the production of  $OMB^{\cdot+}$  and

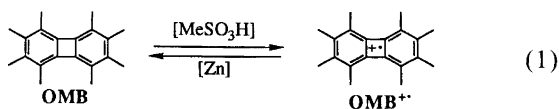
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related radical cations in nearly quantitative yields. In **Part 2**, catalytic benzylic coupling, epoxide and pinacol rearrangement, and stilbene isomerization by both proton-transfer and electron-transfer procedures are examined under otherwise identical reaction conditions.

### Part 1

Direct (one-electron oxidation) of neutral organic donors (D) by dissolution in Brønsted acids such as sulfuric acid or trifluoroacetic acid, has been a well accepted method for the production of cation-radicals (D<sup>•+</sup>) in solution, especially for EPR spectroscopy.<sup>26,27</sup> Despite the extensive use of acids, experimental evidence for how the oxidation occurs is lacking.<sup>28</sup>

**I. Oxidation of octamethylbiphenylene to its cation-radical by Brønsted acids.** Addition of freshly distilled methanesulfonic acid to a 0.2 mM solution of octamethylbiphenylene in dichloromethane, immediately resulted in a bright blue solution at 25 °C under an argon atmosphere. The UV–VIS spectral analysis of the blue solution revealed an absorption band centered at  $\lambda_{\text{max}} = 602$  nm (shoulder at 550 nm),  $\epsilon = 12020 \text{ M}^{-1} \text{ cm}^{-1}$ .<sup>29</sup> The characteristic twin absorption band was readily assigned to the octamethylbiphenylene cation-radical (OMB<sup>•+</sup>) by comparison with the reported spectral data.<sup>30</sup> Similarly, the solutions of other Brønsted acids such as *p*-toluenesulfonic acid, trifluoroacetic acid, tetrafluoroboric acid, and trifluoromethanesulfonic acid when added to octamethylbiphenylene in dichloromethane, produced the same characteristic blue coloration of OMB<sup>•+</sup>. Qualitatively, the rate of appearance of the blue coloration depended on the strength and amounts of added Brønsted acid. For example, the blue color of OMB<sup>•+</sup> appeared immediately in the presence of 1% methanesulfonic acid, whereas it took several minutes (> 10 min) in the presence of trifluoroacetic acid before any coloration could be detected by UV–VIS spectroscopy. In order to quantify the amount of octamethylbiphenylene cation-radical formed, a dichloromethane solution of OMB containing excess methanesulfonic acid was monitored by UV–VIS spectroscopy. Interestingly, the cation-radical OMB<sup>•+</sup> was rapidly formed in 66% yield within 1 min, but no further change was noted for 30 min (Fig. 1). When the reaction mixture was quenched with solid sodium carbonate, followed by Zn dust, it yielded a pale yellow solution from which neutral octamethylbiphenylene was recovered in quantitative yield.



**II. Protonation and reduction of tetraanisylethylene to its cation-radical.** When a colorless solution of tetra-

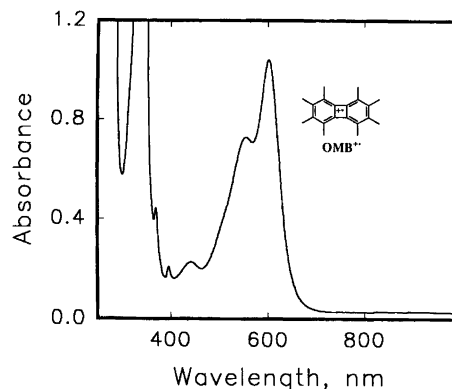
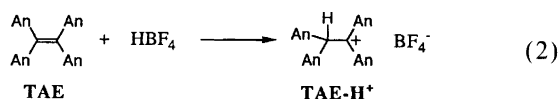
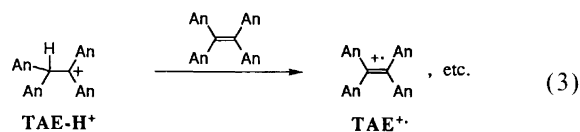


Fig. 1. UV–VIS absorption spectrum of OMB<sup>•+</sup> from the oxidation of octamethylbiphenylene (OMB) with methanesulfonic acid (10% v/v) in dichloromethane at 25 °C.

anisylethylene was treated with excess tetrafluoroboric acid in dichloromethane, it immediately resulted in a dark red solution. UV–VIS spectral analysis of the red solution showed a broad absorption band with a maximum at  $\lambda_{\text{max}} = 508$  nm which was readily assigned to the carbocation, i.e., eqn. (2), by comparison with the



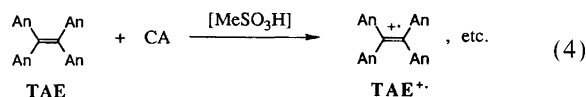
absorption spectra ( $\lambda_{\text{max}} = 505$  nm) previously observed of protonated 1,1-dianisylethylene.<sup>31</sup> The same spectral transformation was observed with methanesulfonic acid and trifluoromethanesulfonic acid. These solutions of the carbocation (in excess of acids) were stable for prolonged periods without any indication of cation-radical formation as monitored by UV–VIS spectroscopy. However, the further addition of neutral tetraanisylethylene to the dark red solution of the carbocation immediately resulted in the characteristic blue coloration of tetraanisylethylene cation-radical ( $\lambda_{\text{max}} = 565$  and 926 nm),<sup>32</sup> eqn. (3).



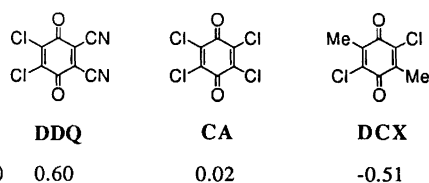
**III. Quantitative oxidation of organic donors to their cation-radicals by Brønsted acids in the presence of quinones.**

**A. Oxidation of tetraanisylethylene (TAE).** When tetraanisylethylene in dichloromethane was treated with methanesulfonic acid in the presence of chloranil, the characteristic blue coloration of tetraanisylethylene cation-radical ( $\lambda_{\text{max}} = 565$  and 926 nm) was observed immediately, eqn. (4).

The same coloration was observed when tetraanisylethylene was treated with methanesulfonic acid in the presence of other quinones such as 2,3-dichloro-

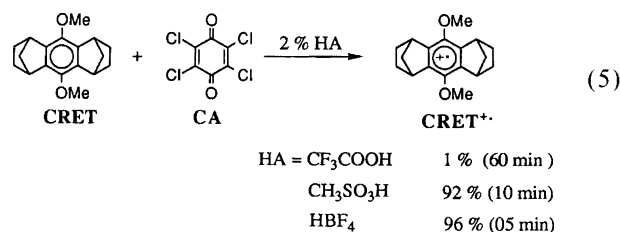


5,6-dicyanobenzoquinone (DDQ) or 2,5-dichloro-*p*-xyloquinone (DCX). The spectrophotometric analysis of the blue solutions revealed that all the quinones in Scheme 1 produced nearly quantitative yields of TAE<sup>+</sup> within 5 min, despite large differences in the reduction potentials of these quinones ( $\approx 1.1$  V in Scheme 1). In a control experiment, a dichloromethane solution of tetraanisylethylene and methanesulfonic acid without added chloranil, immediately led to a red colored solution of the protonated tetraanisylethylene cation (*vide supra*). However, only traces (<1%) of TAE<sup>+</sup> were produced during a 5 min period. Thus these experiments clearly indicated that the oxidation of TAE by methanesulfonic acid was strongly accelerated by the presence of quinones. Moreover, similar acceleration of tetraanisylethylene oxidation was observed with quinones and other Brønsted acids (CF<sub>3</sub>COOH, HBF<sub>4</sub>, etc.).



Scheme 1.

**B. Stoichiometric oxidation of aromatic ethers to their cation-radicals.** A solution of a hydroquinone ether CRET (0.21 mM) and chloranil (0.5 mM) in dichloromethane was treated with 2% trifluoroacetic acid. The color of the solution remained unchanged for several min and spectral analysis of the solution showed cation-radical (*orange* CRET<sup>+</sup>) to be present in less than <1% yield (during the course of 1 h). However, when trifluoroacetic acid was replaced with stronger acids (either methanesulfonic or tetrafluoroboric acid), the solution showed a rapid growth of *orange* CRET<sup>+</sup> (Fig. 2), to attain a nearly quantitative yield (based on added neutral CRET).



**C. Isolation of *orange* CRET<sup>+</sup> using chloranil and HBF<sub>4</sub>.** Since the high yields of cation-radical with various donors were obtained in solution [eqn. (5)], we further

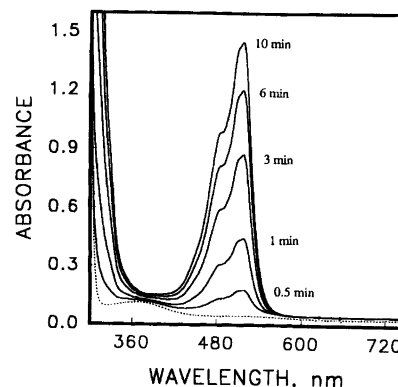
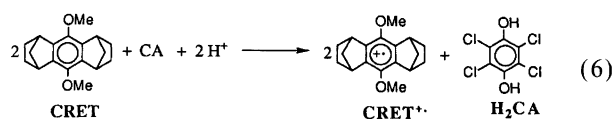


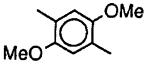
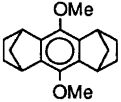
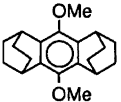
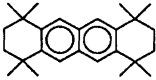
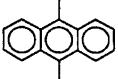
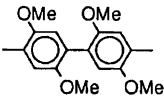
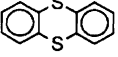
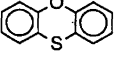
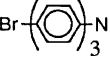


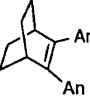
Fig. 2. Temporal evolution of *orange* CRET<sup>+</sup> from the treatment of 0.21 mM neutral CRET with methanesulfonic acid (2% v/v) and 0.5 mM chloranil in dichloromethane. The dashed curve is the spectrum of chloranil and methanesulfonic acid alone.

attempted the isolation of the crystalline *orange* CRET<sup>+</sup> as follows. A mixture of CRET (1 mmol, 0.1 M) and chloranil (1.2 mmol) in dichloromethane was stirred at 25 °C under an argon atmosphere. When a solution of HBF<sub>4</sub>·Et<sub>2</sub>O in dichloromethane was added to the vigorously stirred mixture, the reaction mixture immediately turned deep orange red. The highly colored mixture was cooled to 0 °C and prechilled anhydrous diethyl ether was added. The deep orange precipitate of *orange* CRET<sup>+</sup> BF<sub>4</sub><sup>-</sup> thus formed was filtered under an argon atmosphere and dried *in vacuo* (0.87 mmol). The purity of the crystalline *orange* CRET<sup>+</sup> BF<sub>4</sub><sup>-</sup> determined iodometrically<sup>33</sup> was found to be greater than 98%. The analysis of the ethereal filtrate (after washing with water) yielded neutral CRET (0.12 mmol), chloranil (0.76 mmol) and hydrochloranil (0.43 mmol). The identity of hydrochloranil (H<sub>2</sub>CA) was further confirmed by isolation as the diacetate derivative (see the Experimental section). The stoichiometry of the oxidation of CRET using chloranil and HBF<sub>4</sub> can thus be represented as eqn. (6).



**D. Oxidation of other organic donors to their cation-radicals.** A variety of aromatic, heteroatom-centered, and olefinic electron donors were rapidly oxidized to the corresponding cation-radicals in excellent yields (Table 1), using a solution of methanesulfonic acid and chloranil in dichloromethane at 25 °C. Note that the high quality UV-VIS absorption spectra of various cation-radicals presented in Fig. 3 were identical with those obtained either by electrochemical (anodic) or chemical oxidation (NO<sup>+</sup> BF<sub>4</sub><sup>-</sup> or *orange* CRET<sup>+</sup> SbCl<sub>6</sub><sup>-</sup>) of various donors in Table 1 (see the Experimental section).

Table 1. Oxidation of various electron donors to their cation-radicals by methanesulfonic acid in the presence of chloranil.<sup>a</sup>

Donor (D)	$E_{1/2}/V$ vs. SCE <sup>b</sup>	Cation-radical	
		$\lambda_{\max}(\log \epsilon)^c$	% Yield <sup>d</sup>
	1.01	464 (4.02), 448sh	97
	1.11	5.18 (3.86), 486sh	92
	1.30	486 (3.66), 464sh	88
	1.35	672 (3.68), 616, 546 <sup>e</sup>	78
	1.22	670 (4.02) <sup>e</sup>	93
	1.19	584 (3.99), 418	82
	1.21	540 (4.08)	91
	1.19	584 (4.09)	94
	1.12	728 (4.45)	92
	0.80	560 (4.28), 926	98
	1.12	516 (4.18), 885	98
	0.98	546 (4.16), 880	97

<sup>a</sup>In dichloromethane containing 2% (v/v) MeSO<sub>3</sub>H and 0.1 mM CA and 0.2–0.5 mM donor at 25 °C under an argon atmosphere.

<sup>b</sup>In dichloromethane solution containing 0.2 M *n*-Bu<sub>4</sub>N<sup>+</sup> PF<sub>6</sub><sup>-</sup> at  $v=100$  mV s<sup>-1</sup> and 25 °C. <sup>c</sup> $\lambda_{\max}$  in nm and  $\log \epsilon_{\max}$  in M<sup>-1</sup> cm<sup>-1</sup>. <sup>d</sup>Spectra were recorded 20 min after the mixing of the reagents. <sup>e</sup>For other absorption bands see Fig. 3.

IV. Unified view of the facile conversion of organic donors by Brønsted acids. The oxidative conversion of octamethylbiphenylene, tetraanisylethylene, and related aromatic donors into their cation-radicals by Brønsted

acids as described into sections A–D above, conveyed to us a consistent theme of the ready interconversion of diamagnetic and paramagnetic intermediates. In order to facilitate the combined analysis, let us generically

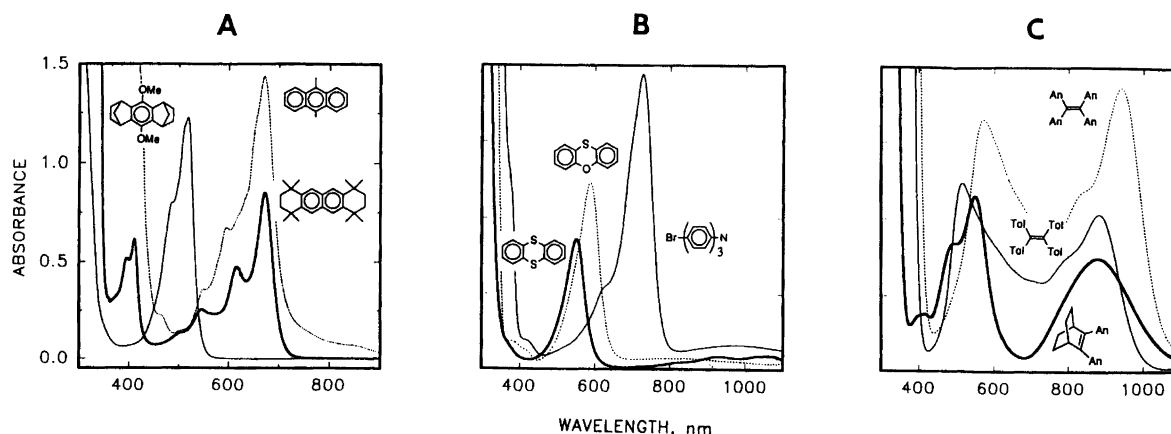
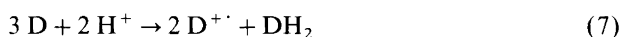


Fig. 3. UV-VIS absorption spectra of various cation-radicals from (A) aromatic, (B) heteroatom-centered, and (C) olefin donors, as indicated, by treatment of 0.1–0.2 mM solutions with methanesulfonic acid (2% v/v) and 0.5 mM chloranil in dichloromethane at 24 °C, and recorded 20 min after mixing the reactants.

designate all donors as D and their cation-radicals as  $D^{+\cdot}$  in the following way.

**A. Octamethylbiphenylene cation-radical ( $OMB^{+\cdot}$ ).** We suggest that the rapid formation of  $OMB^{+\cdot}$  to attain a critical conversion of 66% in eqn. (1) is diagnostic of a 3:2 stoichiometry, eqn. (7),



where  $DH_2$  is the dihydro derivative deduced from the previous studies of Hart and coworkers.<sup>34</sup> If so, the initial protonation of octamethylbiphenylene can be followed by the series of electron- and proton-transfer steps to yield the characteristic 3:2 stoichiometry in eqn. (7), i.e., eqns. (8)–(11) in Scheme 2, where D=octamethylbiphenylene. According to Scheme 2, the acid strength plays a critical role in the proton-transfer steps (8) and (10) (especially the latter), and the donor strength of D is relevant to the electron-transfer steps in eqns. (9) and (11).



Scheme 2.

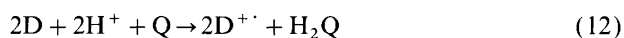
**B. Tetraanisylethylene cation-radical.** The validity of the electron-transfer step in eqn. (9), Scheme 2, is independently confirmed by the appearance of tetraanisylethylene cation-radical ( $TAE^{+\cdot}$ ) in eqn. (3). As such, the formation of  $TAE^{+\cdot}$  from tetraanisylethylene and strong acids such as  $HBF_4$  or  $CF_3SO_3H$  follows from the proton-transfer/electron-transfer sequence observed in eqns. (2) and (3) (Scheme 3), where D=tetraanisylethylene.



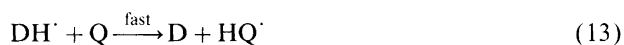
Scheme 3.

Depending on the fate of the tetraanisylethylene radical  $DH^{\cdot}$  in the acidic medium, the conversion into the cation-radical ( $TAE^{+\cdot}$ ) may or may not reach steady-state.<sup>35</sup>

**C. Aromatic cation-radicals.** Full (>95%) conversion into the cation-radical in Scheme 3 can be easily achieved in the presence of an oxidant such as the quinone (Q) in eqn. (4) and Table 1. Most notably, the essentially quantitative yields of  $D^{+\cdot}$  are achieved by the concomitant reduction of the quinone according to the stoichiometry in eqn. (6), i.e., eqn. (12),



where  $H_2Q$ =hydroquinone. Such 1:1 stoichiometry of the donor and the acid derives from Scheme 3 via the rapid oxidation of the radical  $DH^{\cdot}$  by quinone and accompanying shift of equilibrium 9, Scheme 4, where the hydroquinone  $H_2Q$  in eqn. (12) is stoichiometrically equivalent to  $HQ^{\cdot}$  (plus a hydrogen)<sup>36</sup> in eqn. (13). It is particularly noteworthy that the facile oxidation in [eqn. (13)] Scheme 4 accounts for the essentially quantitative yields of the cation-radical that are obtained from eqn. (4), irrespective of the base strength or reduction potential of the quinones in Scheme 1 (despite a span of more than 25 kcal mol<sup>-1</sup> in driving force). Furthermore, the tetraanisylethylene that is relatively readily protonated<sup>37</sup> in eqn. (8) is even oxidized by the weaker trifluoroacetic acid when quinone is present. By contrast, aromatic donors (as rather poor proton acceptors) are strongly dependent on the strength of added acid in the quinone-mediated oxidative conversion into cation radicals (Table 1).



Scheme 4.

Taken together, we believe that Schemes 2–4 present

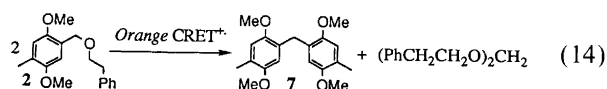
a consistent pattern of facile proton- and electron-transfer processes that readily interconvert diamagnetic cations and paramagnetic radical/cation-radicals from octamethylbiphenylene, tetraanisylethylene and the various donors listed in Table 1.

## Part 2

Comparative studies of electron-transfer catalysis and proton-transfer catalysis were carried out under reaction conditions that were identical in solvent, temperature, light, etc. Otherwise, we chose tetrafluoroboric acid as the acid catalyst and *orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$  as the electron-transfer catalyst for the following reason. It has been suggested that cation-radical catalyzed reactions are, in fact, disguised acid-catalyzed processes, in which the acid is produced by deprotonation of the cation-radical or by its reaction with adventitious water.<sup>24,25</sup> We therefore conjectured that the decomposition of *orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$  (and other cation-radicals) would lead to tetrafluoroboric acid as the decomposition product. Accordingly, the catalytic procedures with *orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$  and  $\text{HBF}_4$  are described as follows.

### I. Catalytic synthesis of diphenylmethanes via benzylic coupling.

A. *Electron-transfer.* The dealkylative coupling of benzyl alkyl ethers to the corresponding diphenylmethanes according to the stoichiometry in eqn. (14) can be readily brought about with either catalytic amounts of a mild



one-electron oxidant (such as *orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$ ) or by an equivalent electrochemical method.<sup>25c</sup> Thus when a colorless solution of 4-methyl-2,5-dimethoxybenzyl alkyl ether (**2**) in dichloromethane was treated at 0 °C with a small amount (1%) of purified *orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$  (see Experimental section), the reaction mixture turned bright yellow immediately. The spectrophotometric analysis of the yellow solution showed a characteristic absorption band with  $\lambda_{\text{max}} = 460 \text{ nm}$  and a shoulder at  $\approx 440 \text{ nm}$  and it was assigned to the cation-radical of benzyl ether,  $2^{+\cdot}$ , by comparison with the spectrum of the parent 2,5-dimethyl-1,4-dimethoxybenzene cation-radical.<sup>38</sup> On continued stirring for half an hour, the yellow solution developed a slight green coloration. In a simple work-up procedure, the reaction mixture was treated with zinc dust under an argon atmosphere, followed by filtration. The removal of the solvent *in vacuo* afforded the corresponding diarylmethane **7** and bis(2-phenylethoxy)methane in 100 and 85% yields, respectively, according to the stoichiometry in eqn. (14). Based on the amount of added *orange*  $\text{CRET}^{+\cdot}$ , the yield of diarylmethane **7** was in excess of 10 000%. The role of a cation-radical intermediate in the dealkylative coupling

of benzyl alkyl ethers, was further confirmed by efficient interruption of the catalytic chain process with various electron-transfer quenchers such as octamethylbiphenylene, iodide, and zinc dust.

Application of the same procedure to benzyl alkyl ethers **1–4** led to the corresponding diarylmethanes in good to excellent yields, as listed in Table 2. It is noteworthy that the fully substituted benzyl methyl ether **5** afforded only traces of the corresponding diarylmethane (**10**), even after stirring the reaction mixture for prolonged periods (12 h). Moreover, the relatively less-substituted ether **6** (Table 2) was found to be similarly unreactive under these conditions (*vide infra*).

B. *Acid catalysis of the dealkylative coupling of benzyl alkyl ethers.* We next examined the efficacy of the dealkylative coupling of benzyl alkyl ethers in the presence of a catalytic amount of tetrafluoroboric acid. Thus, a prechilled ( $\approx 0 \text{ }^\circ\text{C}$ ) colorless solution of benzyl methyl ether **1** in anhydrous dichloromethane was treated with a catalytic amount (1%) of  $\text{HBF}_4$  (as an etherate complex) without any perceptible color change. The reaction was stirred at 0 °C for  $\approx 50 \text{ min}$ , and was quenched with saturated aqueous sodium bicarbonate solution. The simple removal of the solvent *in vacuo* led to a quantitative yield of diarylmethane **7** (Table 2).

The same procedure was effective in catalyzing the dealkylative coupling of benzyl alkyl ethers **1–4** in excellent yields, as listed in Table 2. Interestingly, the fully substituted ether **5** afforded only traces of diarylmethane **10**, even after stirring the reaction mixture for 4 h. It is noteworthy that the dealkylative coupling of same benzyl ether **5** was similarly ineffective with *orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$  salt.

C. *Electron-transfer catalysis with nitrosonium tetrafluoroborate.* The dealkylative coupling of benzyl alkyl ethers could also be carried out with commercially available one-electron oxidants, such as the nitrosonium tetrafluoroborate salt ( $\text{NO}^+ \text{BF}_4^-$ ).<sup>30b</sup> For example, the addition of a few crystals of  $\text{NO}^+ \text{BF}_4^-$  ( $\approx 1\%$ ) to a dichloromethane solution of **2** under an argon atmosphere at 0 °C led to the characteristic yellow coloration of benzyl ether cation-radical ( $2^{+\cdot}$ ). Excellent yields of corresponding diarylmethane **7** and bis-(2-phenylethoxy)methane were obtained based on the stoichiometry depicted in eqn. (14). Interestingly, the electron-poor benzyl methyl ether **5** [which was very inefficiently catalyzed by either *orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$  or  $\text{HBF}_4$  (*vide supra*)], when treated with a catalytic amount of  $\text{NO}^+ \text{BF}_4^-$  salt in anhydrous dichloromethane, furnished the corresponding diarylmethane **10** quantitatively according to eqn. (15).

Similar treatment of relatively unsubstituted benzyl

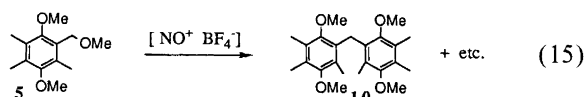
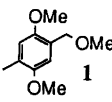
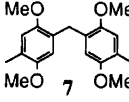
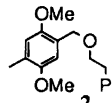
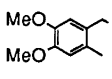
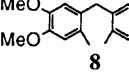
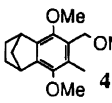
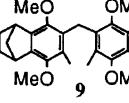
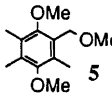
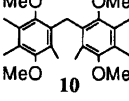
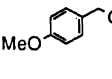
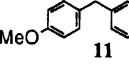


Table 2. Catalysis of the benzylic coupling of benzyl alkyl ethers with either *orange* CRET<sup>++</sup> BF<sub>4</sub><sup>-</sup> and HBF<sub>4</sub>·OEt<sub>2</sub> in dichloromethane.<sup>a</sup>

Benzylalkyl ether	$E_{1/2}$ / V vs. SCE <sup>b</sup>	Product	<i>orange</i> CRET <sup>++</sup>		HBF <sub>4</sub> ·OEt <sub>2</sub>	
			<i>t</i> /h	Yield <sup>c</sup> (%)	<i>t</i> /h	Yield <sup>c</sup> (%)
	1.17		0.5	(96)	0.8	(96)
	1.16	<b>7</b>	0.4	(96) <sup>d</sup>	0.8	(96)
	1.25		2.0	(96)	3.0	(96)
	1.24		2.5	(87)	3.0	(87)
	1.51		12.0 4.0	(<2) <sup>e</sup> (94) <sup>f</sup>	3.0	(<2)
	1.63		12.0 4.0	(<5) <sup>e</sup> (92) <sup>f</sup>	4.0	(<2)

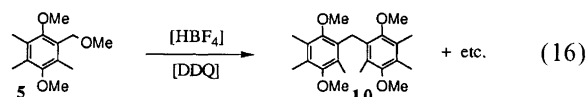
<sup>a</sup>A 0.1 M solution of benzyl alkyl ether containing 1 mol% *orange* CRET<sup>++</sup> or HBF<sub>4</sub>·OEt<sub>2</sub> in dichloromethane at 0 °C unless otherwise indicated. <sup>b</sup>In dichloromethane containing 0.2 M tetrabutylammonium hexafluorophosphate. <sup>c</sup>Isolated yields. <sup>d</sup>Bis(2-phenylethoxy)methane isolated in 82% yield. <sup>e</sup>Starting material recovered. <sup>f</sup>1 mol% NO<sup>+</sup> BF<sub>4</sub><sup>-</sup> as the catalyst to replace *orange* CRET<sup>++</sup>.

ether **6** with a catalytic amount of nitrosonium salt readily afforded the corresponding dianisylmethane **11** in excellent yield (Table 2).

*D. Catalysis of the dealkylative coupling of benzyl methyl ether 5 with catalytic amounts of quinone and HBF<sub>4</sub>.* The deactivated benzyl ethers **5** and **6** did not undergo efficient dealkylative coupling in the presence of either *orange* CRET<sup>++</sup> BF<sub>4</sub><sup>-</sup> or tetrafluoroboric acid (*vide supra*), but a catalytic amount of nitrosonium tetrafluoroborate, a strong one-electron oxidant, readily effected the dealkylative coupling.

The efficient oxidation of aromatic donors with Brønsted acids in the presence of quinones, prompted us to examine the effect of added quinone (such as DDQ) on dealkylative coupling of benzyl ethers in dichloromethane containing 1% HBF<sub>4</sub>. Thus, a solution of the benzyl ether **5** in dichloromethane containing HBF<sub>4</sub> (1%) was treated with a catalytic amount (1%) of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) at 0 °C. The solution immediately took on a pale brown coloration and the resulting mixture was stirred for 3 h. The reaction mixture

was quenched with aqueous sodium bicarbonate, and the dichloromethane layer was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* and chromatographic purification afforded the diarylmethane **10** in 65% yield, eqn. (16). When the benzyl ether **5** alone was treated with catalytic amounts of DDQ (1%) in a control experiment at 0 °C, only the unchanged benzyl ether **5** was recovered after 3 h.

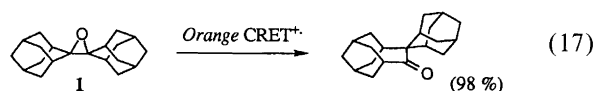


*II. Catalytic rearrangement of epoxides to ketones.* Substituted olefin oxides are known to undergo rapid pinacol rearrangement to the corresponding ketones in the presence of acidic catalysts. On the other hand, Lopez and Troisi<sup>18</sup> and others<sup>19</sup> have noted that epoxides are also readily rearranged to ketones in the presence of

catalytic amounts of oxidants such as ‘magic blue’ and trityl hexachloroantimonate salts. The similarity in acid-catalysis versus electron-transfer catalysis in the rearrangement of epoxides prompted us to examine the efficacy of this rearrangement with the one-electron oxidant (*orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$ ), and compare it with acid catalysts (tetrafluoroboric acid) as follows.

#### A. Electron-transfer catalysis of epoxide rearrangement.

The rearrangement of the epoxides to ketones was readily effected by catalytic amounts of one-electron oxidants such as *orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$ . For example, a 0.1 M solution of the adamantylideneadamantane oxide **1** in anhydrous dichloromethane was treated with a catalytic amount of a purified crystalline sample of *orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$  (1%) at 0 °C. The solution immediately took on a bright orange-red coloration, and it was monitored by UV-VIS spectroscopy. The orange-red solution did not show a decrease in the absorbance at the monitoring wavelength of  $\lambda_{\text{max}} = 518 \text{ nm}$ . The orange solution remained unchanged during the course of the reaction (2 h) as monitored periodically by UV-VIS spectroscopy. Since there was no visible color change, the progress of the reaction was monitored by GC and GC-MS analysis by periodically removing an aliquot of the reaction mixture (see the Experimental section). In a typical work-up procedure, the reaction was quenched with zinc dust. After the orange color had been completely bleached, the heterogeneous mixture was filtered and the solvent was removed *in vacuo*. Analysis of the solid residue showed a quantitative yield of the rearranged ketone and neutral CRET. Furthermore, the chromatographic purification of the solid residue afforded the pure ketone in 96% (isolated) yield.

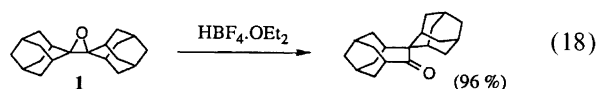


Importantly, the catalytic chain process for eqn. (17) was effectively interrupted by the addition of either octamethylbiphenylene or zinc dust. For example, in a similar experiment, a mixture of epoxide **1** and a catalytic amount of *orange*  $\text{CRET}^{+\cdot}$  in dichloromethane was prepared at 0 °C and stirred for 2 min. A solution of octamethylbiphenylene in anhydrous dichloromethane was then added. The solution immediately turned dark blue and the spectral (UV-VIS) analysis confirmed the presence of octamethylbiphenylene cation-radical (*vide supra*). The reaction mixture was stirred for 3 h and zinc dust was added. After stirring for an additional 5 min, the reaction mixture was worked up (as described above) to afford a viscous residue which, upon GC analysis, indicated only partial conversion of epoxide **1** into the rearranged ketone **10** ( $\approx 5\%$ ). The remainder of the epoxide was recovered unchanged. Similar inhibition by zinc dust afforded 3% of rearranged ketone and the remainder of starting material was recovered intact.

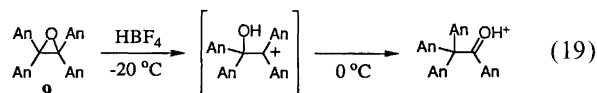
With the procedure described above, a variety of epoxides were converted into the rearranged ketones in excellent yields as listed in Table 3. Qualitatively, the epoxides substituted by the electron-rich anisyl group reacted much more rapidly compared with the corresponding phenyl- or tolyl-substituted epoxides (compare entries **4**, **6**, and **9** with **3**, **5**, and **7** in Table 3).

#### B. Acid-catalyzed rearrangement of epoxides.

The rearrangement of various epoxides in Table 3 was catalyzed equally well by replacing *orange*  $\text{CRET}^{+\cdot} \text{BF}_4^-$  with tetrafluoroboric acid, under otherwise identical reaction conditions (Table 3). Thus, a solution of adamantylideneadamantane oxide **1** in dichloromethane at 0 °C was treated with 1 mol% of tetrafluoroboric acid. The pale yellow mixture was stirred for 1.5 h, and work-up afforded the pure rearranged ketone **10** in 96% isolated yield, eqn. (18).



In another experiment, a solution of tetraanisylethylene oxide **9** in dichloromethane at  $-20 \text{ }^\circ\text{C}$  (in an ice-acetone bath) was treated with catalytic amount of  $\text{HBF}_4 \cdot \text{OEt}_2$ . The solution immediately turned deep red, and the UV-VIS spectral analysis showed an absorption band at  $\lambda_{\text{max}} = 538 \text{ nm}$  (Fig. 4) which was quite characteristic of dianisylalkyl cation (*vide supra*). Thus, protonation of the epoxide **9** followed by ring opening would lead to the dianisylalkyl cation, eqn. (19).



When the deep red solution was warmed to  $\approx 0 \text{ }^\circ\text{C}$ , it yielded a pale yellow solution which upon spectral exam-

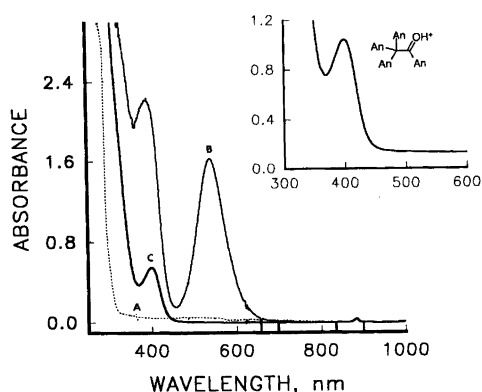


Fig. 4. Spectral changes attendant upon the treatment of (A) 0.1 mM tetraanisylethylene oxide in dichloromethane at  $-20 \text{ }^\circ\text{C}$ . (B) Same solution after the addition of 0.01 mM  $\text{HBF}_4$ . (C) On warming (B) to  $24 \text{ }^\circ\text{C}$ . Inset shows (C) to be the same as the spectrum of the ketone conjugate acid prepared from 0.01 mM (rearranged) anisylpinacolone and 0.1 mM  $\text{HBF}_4$ .



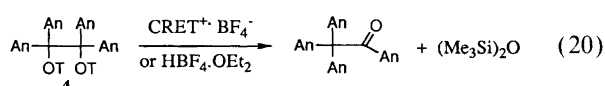
Table 3. Catalysis of the rearrangement of epoxides to the corresponding ketones using *orange*  $\text{CRET}^{++} \text{BF}_4^-$  and  $\text{HBF}_4 \cdot \text{OEt}_2$  in dichloromethane.<sup>a</sup>

Epoxide	Ketone	<i>orange</i> $\text{CRET}^{++}$		$\text{HBF}_4 \cdot \text{OEt}_2$	
		t/h	Yield <sup>b</sup> (%)	t/h	Yield <sup>b</sup> (%)
		2.0	(98)	1.5	(96)
		<0.1	(100)	<0.1	(97)
		1.5	(98)	1.0	(94)
3. Ar = C <sub>6</sub> H <sub>5</sub> 4. Ar = 4-MeOC <sub>6</sub> H <sub>4</sub>	13. Ar = 4-MeOC <sub>6</sub> H <sub>4</sub>	<0.1	(97)	<0.1	(95)
		1.0	(96)	0.6	(97)
5. Ar = 4-MeC <sub>6</sub> H <sub>4</sub> 6. Ar = 4-MeOC <sub>6</sub> H <sub>4</sub>	15. Ar = 4-MeOC <sub>6</sub> H <sub>4</sub>	<0.1	(99)	<0.1	(98)
		1.0	(97)	0.5	(96)
7. Ar = C <sub>6</sub> H <sub>5</sub> 8. Ar = 4-MeC <sub>6</sub> H <sub>4</sub> 9. Ar = 4-MeOC <sub>6</sub> H <sub>4</sub>	17. Ar = 4-MeC <sub>6</sub> H <sub>4</sub> 18. Ar = 4-MeOC <sub>6</sub> H <sub>4</sub>	0.5 <0.1	(99) (99)	0.2 <0.1	(99) (98)

<sup>a</sup>A 0.1 M solution of epoxide containing 1 mol% *orange*  $\text{CRET}^{++}$  or  $\text{HBF}_4 \cdot \text{OEt}_2$  in dichloromethane at 0 °C unless otherwise indicated. <sup>b</sup>Isolated yields.

ination indicated a UV–VIS absorption band at  $\lambda_{\text{max}} = 396$  nm indicative of the protonated rearranged ketone [eqn. (19)]. Note that the same absorption spectrum ( $\lambda_{\text{max}} = 396$  nm) was obtained when a solution of the authentic rearranged ketone in dichloromethane was mixed with 1 mol%  $\text{HBF}_4$  (see inset of Fig. 4).

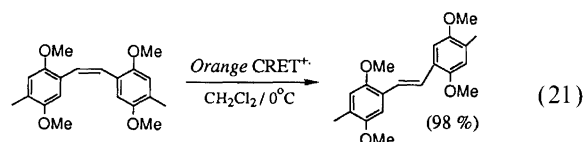
**III. Catalysis of the pinacol–pinacolone rearrangement.** In a similar vein, the various silylated pinacols listed in Table 4 were readily rearranged to the corresponding pinacolones in excellent yields, when catalyzed either by 1 mol% *orange*  $\text{CRET}^{++} \text{BF}_4^-$  or  $\text{HBF}_4$  at 0 °C in dichloromethane, under similar reaction conditions.



Moreover, no C–C bond cleavage product that corresponded to either the acetophenone or benzophenone was detected. The *orange*  $\text{CRET}^{++}$  catalyzed pinacol–pinacolone rearrangement was subject to complete inhibi-

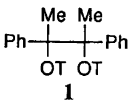
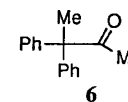
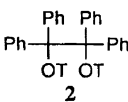
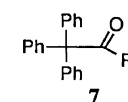
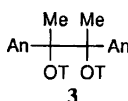
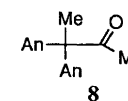
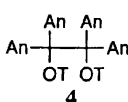
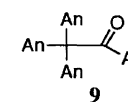
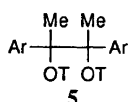
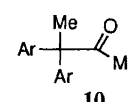
tion by added octamethylbiphenylene or zinc dust (see the Experimental section).

**IV. cis–trans Isomerization of stilbene.** *cis–trans* Isomerization of the stilbenes could be readily carried out using catalytic amounts of Brønsted acid or under oxidizing conditions. For example, the *cis–trans* isomerization of the electron-rich *cis*-stilbene<sup>39</sup> to the corresponding *trans*-isomer was effected in dichloromethane in the presence of a small (0.1 mol%) amount of *orange*  $\text{CRET}^{++} \text{BF}_4^-$  within 10 min in excellent yield (see the Experimental section). The latter corresponded to a catalytic turnover of 1000.



The same isomerization in eqn. (21) was also achieved with 1 mol% of  $\text{HBF}_4$  in dichloromethane at 0 °C (20 min) to afford the *trans* olefin in 98% isolated yield.

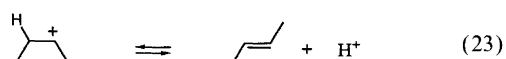
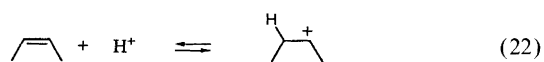
Table 4. Catalytic rearrangement of silylated pinacols to pinacolones using *orange* CRET<sup>++</sup> BF<sub>4</sub><sup>-</sup> and HBF<sub>4</sub>·OEt<sub>2</sub> in dichloromethane.<sup>a</sup>

Silylated pinacol	Pinacolone	<i>orange</i> CRET <sup>++</sup>		HBF <sub>4</sub> ·OEt <sub>2</sub>	
		t/h	Yield <sup>b</sup> (%)	t/h	Yield <sup>b</sup> (%)
 1	 6	2.0	(99)	1.5	(96)
 2	 7	1.0	(97)	0.6	(98)
 3	 8	0.2	(98)	<0.1	(94)
 4	 9	<0.1	(96)	<0.1	(94)
 5	 10	<0.1	(96)	<0.1	(97)

OT = OSiMe<sub>3</sub>, Ph = C<sub>6</sub>H<sub>5</sub>, An = 4-MeOC<sub>6</sub>H<sub>4</sub>, Ar = 3,4-(OMe)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>. <sup>a</sup>A 0.1 M solution of silylated pinacol containing 1 mol% *orange* CRET<sup>++</sup> or HBF<sub>4</sub>·OEt<sub>2</sub> in dichloromethane at 0 °C under an argon atmosphere. <sup>b</sup>Isolated yields.

## Discussion

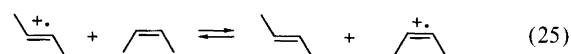
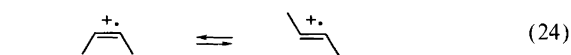
The benzylic coupling in eqns. (14)–(16), the epoxide/pinacolic rearrangements in eqns. (17)–(20) and *cis*–*trans* isomerization described in eqn. (21) are all subject to acid catalysis as well as electron-transfer catalysis – with results that are *remarkably comparable*. Accordingly, let us first focus on the simple *cis*–*trans* isomerization in eqn. (21), in which acid catalysis proceeds via the carbocationic intermediate (DH<sup>+</sup>) in Scheme 5, where the olefin represents the donor D in



Scheme 5.

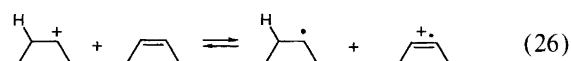
Scheme 3. On the other hand, electron-transfer catalysis involves the prior one-electron oxidation of the olefin to its cation-radical (D<sup>•+</sup>). For the catalytic sequence, the facile isomerization of the labile cation-radical [eqn. (24)] is followed by electron transfer with the olefin donor [eqn. (25)].

As cleanly as these processes can be conceptually delineated – one proceeding via diamagnetic cations and



Scheme 6.

the other via paramagnetic cation-radicals\* – in practice the pathways could intersect. For example, the carbocation relevant to acid catalysis (Scheme 5) is subject to electron-transfer with the olefin (D), as observed in eqn. (3) [and described by eqn. (9)], i.e. eqn. (26).



In such an event, the cation-radical is free to then engage in the ETC manifold (Scheme 6). Conversely, if the first-formed-olefin cation-radical (D<sup>•+</sup>) in electron transfer catalysis (Scheme 6) is subject to deprotonation (or reacts with adventitious water), the liberated acid is

\*It is important to emphasize the caveat that the spectral observation of a transient species does not by itself prove that it is a reactive intermediate in the catalysis. By the same token if a species is not observed, it does not necessarily rule it out as reactive intermediate.

then free to participate in the proton-transfer manifold (Scheme 5). Thus, the experiments described for the *cis*-*trans* isomerization in eqn. (21) are insufficient to delineate either pathway definitively. The same ambiguity applies to the epoxide/pinacol rearrangements described in eqns. (17)–(20).

The closest we have been able to make any mechanistic distinction between acid catalysis and electron-transfer catalysis lies in the control experiments carried out for the coupling of benzylic ether **5** (and **6**) in eqn. (16). Although the acid catalysis of deactivated ethers **5** and **6** with  $\text{HBF}_4$  is highly inefficient (*vide supra*), the experiment in eqn. (16) shows that a catalytic amount of quinone (DDQ) is required in eqn. (13) to pull the disproportionation equilibrium in eqn. (9) to completion.<sup>40</sup> In other words, this control experiment demonstrates that electron-transfer catalysis is operative under conditions in which acid catalysis is not. At this juncture, we have been unable to design a comparable experiment(s) for the converse situation, *viz.* to demonstrate that acid catalysis is operative under conditions in which electron-transfer catalysis is not. However, we are uncertain at this juncture as to whether such a mechanistic distinction can be generalized.

### Summary and conclusions

We have selected (in **Part 2**) some common organic transformations (sections I–IV) to examine the viability of acid catalysis and electron-transfer catalysis with fluoroboric acid ( $\text{HBF}_4$ ) and cation-radical oxidant (*orange*  $\text{CRET}^+$ ), respectively. The catalytic processes in each case proceed with remarkably comparable facility. Although acid catalysis and electron-transfer catalysis involve diamagnetic carbocations ( $\text{DH}^+$ ) and paramagnetic cation-radicals as ( $\text{D}^{\cdot+}$ ) as different types of reactive intermediate, the facile interchange between  $\text{DH}^+$  and  $\text{D}^{\cdot+}$  as shown by the experiments in **Part 1** allows crossover from one catalytic manifold to the other. As such, a clean mechanistic distinction between acid catalysis and electron-transfer catalysis is very difficult to make with certainty.† Such ambiguity raises the question as to whether previous studies of acid catalysis<sup>1–11</sup> and electron-transfer catalysis<sup>17–22</sup> of organic reactions have adequately ruled out the alternative mechanistic possibility.

### Experimental

**Materials.** The various electron donors such as octamethylbiphenylene (OMB),<sup>23</sup> 2,5-dimethyl-1,4-dimethoxybenzene,<sup>41</sup> 9,10-dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene,<sup>33</sup> 2,2',5,5'-tetramethoxy-4,4'-dimethylbiphenyl,<sup>41</sup> phenoxthin,<sup>42</sup>

1,1,2,2-tetrakis(4-methoxyphenyl)ethylene<sup>43</sup> (tetranisyl-ethylene), 1,1,2,2-tetrakis(4-methylphenyl)ethylene,<sup>19d</sup> 2,3-bis(4-methoxyphenyl)bicyclo[2.2.2]oct-2-ene,<sup>43</sup> and 1,2,3,4,7,8,9,10-octahydro-1,1,4,4,7,7,10,10-octamethylnaphthacene<sup>44</sup> [m.p. 319–321 °C (lit.<sup>44</sup> m.p. 319–320 °C). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  1.36 (s, 24 H), 1.73 (s, 8 H), 7.68 (s, 4 H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  32.55, 34.47, 35.16, 123.98, 130.25, 143.42] were available from the literature procedures. Tetra-*n*-butylammonium hexafluorophosphate, tetra-*n*-butylammonium iodide, 4,4'-dimethoxybiphenyl, 9,10-dimethylantracene, thianthrene, tris(4-bromophenyl)amine, anhydrous *p*-toluenesulfonic acid, methanesulfonic acid, tetrafluoroboric acid–diethyl ether complex, trifluoroacetic acid, and trifluoromethanesulfonic acid were commercially available (Aldrich) and were purified by recrystallization and/or distillation, prior to use. The benzyl alkyl ethers used (Table 2) were prepared by the Williamson method using sodium alkoxides and benzyl halides, obtained from the corresponding arenes using halomethylation reaction,<sup>25d</sup> and the spectral data for various benzyl alkyl ethers have been described previously.<sup>25d</sup> The epoxidation of olefins<sup>43,19d</sup> with *m*-chloroperbenzoic acid in dichloromethane at 25 °C, using a standard procedure,<sup>45</sup> readily afforded the various epoxides in Table 3. Several of these epoxides have been reported previously from this laboratory and were characterized by comparison of the m.p., <sup>1</sup>H and <sup>13</sup>C NMR, and IR data with the reported values,<sup>19d</sup> as well as a GC and GC–MS comparison with the authentic samples, except 2,3-bis(4-methylphenyl)bicyclooctene oxide (**5**) [m.p. 78–79 °C. <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  1.46 (d,  $J=7.8$  Hz, 2 H), 1.82 (d,  $J=8.4$  Hz, 2 H), 2.09 (m, 4 H), 2.30 (s, 6 H), 2.44 (br s, 2 H), 7.02 (d,  $J=8.1$  Hz, 4 H), 7.12 (d,  $J=8.1$  Hz, 4 H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  21.27, 23.91, 25.20, 34.81, 68.70, 127.19, 128.60, 135.25, 136.57. GC–MS: 304, 304 calcd. for  $\text{C}_{22}\text{H}_{24}\text{O}$ ] and 2,3-bis(4-methoxyphenyl)bicyclooctene oxide (**6**) [m.p. 67–68 °C. <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  1.42 (d,  $J=8.1$  Hz, 2 H), 1.78 (d,  $J=8.4$  Hz, 2 H), 2.03 (br m, 4 H), 2.39 (br s, 2 H), 3.74 (s, 6 H), 6.72 (d,  $J=8.7$  Hz, 4 H), 7.08 (d,  $J=8.7$  Hz, 4 H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  23.92, 25.19, 34.76, 55.30, 68.47, 113.31, 128.55, 130.43, 158.58. GC–MS: 336, 336 calcd. for  $\text{C}_{22}\text{H}_{24}\text{O}_3$ ]. The silylated pinacols in Table 4 were prepared according to the literature procedures and were fully characterized by comparison with the reported spectral data.<sup>46</sup> Authentic samples of *cis*- and *trans*-1,2-bis(4-methyl-2,5-dimethoxyphenyl)ethylenes were available from a previous study.<sup>43</sup> The cation-radical *orange*  $\text{CRET}^{\cdot+} \text{BF}_4^-$  was readily isolated as the stable tetrafluoroborate ( $\text{BF}_4^-$ ) salt in quantitative yield from the reaction of hydroquinone methyl ether CRET (9,10-dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene) with nitrosonium tetrafluoroborate.<sup>33</sup> Neutral CRET (precursor for *orange*  $\text{CRET}^{\cdot+}$ ) can be readily synthesized in multigram quantities from the corresponding *bis*-annulated hydroquinone which was easily obtained by the Diels–Alder condensation of *p*-benzoquinone with cyclo-

† Basically, the same ambiguity pertains to base catalysis in relation to electron-transfer catalysis via the Bunnett  $\text{S}_{\text{RN}}1$  mechanism.

pentadiene followed by hydrogenation over palladium-carbon and aromatization with bromine in excellent yield.<sup>33</sup> Nitrosonium tetrafluoroborate (Strem) was stored in a Vacuum Atmospheres HE-493 dry box kept free of oxygen. Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of conc. sulfuric acid ( $\approx 20\%$  by volume) until the acid layer remained colorless. After separation, it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from  $P_2O_5$  under an argon atmosphere and stored in a Schlenk tube equipped with a Teflon valve fitted with Viton O-rings.

**Instrumentation.** The UV-VIS absorption spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer. The  $^1H$  and  $^{13}C$  NMR spectra were recorded on a General Electric QE-300 spectrometer and chemical shifts are reported in ppm units downfield from tetramethylsilane. Gas chromatography was performed on a Hewlett-Packard 5890A series FID gas chromatograph fitted with a model 3392 integrator. GC-MS analyses were carried out on a Hewlett-Packard 5890 chromatograph interfaced to an HP 5970 mass spectrometer (EI, 70 eV).

**Cyclic voltammetry of various electron donors in dichloromethane.** Cyclic voltammetry (CV) was performed on a BAS 100A electrochemical analyzer. The CV cell was of an airtight design with high vacuum Teflon valves and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of an adjustable platinum disk embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without significantly changing the surface area ( $\approx 1 \text{ mm}^2$ ). The saturated calomel electrode (SCE) and its salt bridge was separated from the catholyte by a sintered glass frit. The counter electrode consisted of a platinum wire gauze that was separated from the working electrode by  $\approx 3 \text{ mm}$ . The CV measurements were carried out for solutions of 0.2 M supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate) and  $5 \times 10^{-3} \text{ M}$  electron donor in dry dichloromethane under an argon atmosphere. All the cyclic voltammograms were recorded at a sweep rate of  $100 \text{ mV s}^{-1}$  and were *iR* compensated. The potentials were referenced to SCE which was calibrated with added ferrocene ( $5 \times 10^{-3} \text{ M}$ ). The oxidation potential ( $E_{1/2}$ ) values were the average of the anodic and cathodic peak potentials as listed in Tables 1 and 2.

**General procedure for catalysis by electrochemical oxidation.** The electrooxidations were carried out with a PAR model 173 potentiostat/galvanostat equipped with model 179 digital coulometer which provided a feed-back compensation for ohmic drop between working and the reference electrodes. The voltage-follower amplifier (PAR

model 178) was mounted externally to the potentiostat with a minimum length of high-impedance connection to the reference electrode. The electrochemical cell was of airtight design with high vacuum. The counter electrode was constructed of a double coil of nichrome wire with a large surface area. The working electrode consisted of a platinum-wire cage wrapped with a platinum gauze with a total surface area of  $\approx 1.1 \text{ cm}^2$ . The anodic catalysis of various substrate such as benzyl alkyl ethers, epoxides, and silylated pinacols was carried out at constant potential.

For example, a solution of benzyl alkyl ether **1** in anhydrous dichloromethane (392 mg, 2 mmol, 0.04 M) containing 0.1 M electrolyte (tetra-*n*-butylammonium hexafluorophosphate) was placed in the center compartment of the electrochemical cell. The reference and counter electrode compartments were charged with the dichloromethane containing 0.1 M electrolyte. The mixture was electrolyzed at a constant potential of 1.18 V for 1 min. The current that flowed was recorded by the digitized coulometer to be 0.2 C during this period. The yellow-green solution was stirred for 0.5 h and zinc dust was added. The mixture was stirred for 5 min and filtered. Evaporation of the solvent *in vacuo* left a solid mass which was suspended in hexane and filtered through a short pad of silica gel to afford the diarylmethane **7** (300 mg, 0.95 mmol) in excellent yield (23, 160% based on the amount of current passed through the solution).

**Determination of the extinction coefficient of octamethylbiphenylene cation-radical (OMB<sup>•+</sup>).** The extinction coefficient of OMB<sup>•+</sup> cation-radical reported in the literature ( $\epsilon = 2000 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>23</sup> was found to be erroneous and was corrected to  $\epsilon = 12020 \text{ M}^{-1} \text{ cm}^{-1}$  by employing two independent procedures.

**A. Spectral titration with orange CRET<sup>•+</sup> in dichloromethane.** To a pale yellow solution of OMB (0.12 mM) in dichloromethane (3 ml) was added 50- $\mu\text{l}$  increments of 0.02 mM solution of orange CRET<sup>•+</sup>  $\text{SbCl}_6^-$  ( $\lambda_{\text{max}} = 518 \text{ nm}$ ,  $\epsilon = 7300 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>33</sup> in dichloromethane at 25 °C, under an argon atmosphere. The absorbance change at  $\lambda_{\text{max}} = 602 \text{ nm}$  (due to the formation of OMB<sup>•+</sup> cation-radical) was monitored after the addition of each increment of CRET<sup>•+</sup> solution. A plot of the concentration [CRET<sup>•+</sup>] vs. absorbance change at 602 nm (after appropriate volume corrections) yielded a linear plot with a correlation coefficient greater than 0.999. The slope of the linear plot directly yielded an extinction coefficient of OMB<sup>•+</sup> =  $12020 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$ . The reproducibility of the extinction coefficient was ensured in triplicate runs. The value of extinction coefficient for the OMB<sup>•+</sup> cation radical was further verified by spectral titration with tris(4-bromophenyl)aminium ( $\lambda_{\text{max}} = 728 \text{ nm}$ ,  $\epsilon = 28200 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 9,10-dimethoxy-1,4 : 5,8 - diethano - 1,2,3,4,5,6,7,8 - octahydroanthracene ( $\lambda_{\text{max}} = 486 \text{ nm}$ ,  $\epsilon = 4600 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>33</sup> cation-radicals as hexachloroantimonate salts.

*By electrochemical oxidation.* In an alternative procedure the oxidation of octamethylbiphenylene (5 mM) in dichloromethane solution containing tetra-*n*-butylammonium hexafluorophosphate (0.2 M, as a supporting electrolyte) in a bulk electrolysis apparatus equipped with a 1-cm quartz cuvette, was carried out by passing a known amount of anodic current at a constant potential of 0.8 V. After passage of each increment of current, the blue solution was analyzed by UV-VIS spectroscopy for the absorbance change at  $\lambda_{\max} = 602$  nm. A plot of the amount of current passed vs. the absorbance change (at 602 nm) yielded a linear plot with a correlation coefficient of  $>0.999$ . The slope of the plot yielded the value of extinction coefficient  $\epsilon_{602} = 12\,060\text{ M}^{-1}\text{ cm}^{-1}$ .

Similarly, the extinction coefficients of the various donors listed in Table 1 were determined either by spectral titration using chemical oxidants such as tris(4-bromophenyl)aminium, 9,10-dimethoxy-1,4:5,8-dithano-1,2,3,4,5,6,7,8-octahydroanthracene, and 9,10-dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene (*orange*  $\text{CRET}^{+\cdot}$ ) cation-radicals as hexachloroantimonate salts or by electrochemical oxidation.

*Oxidation of organic donors by Brønsted acids in dichloromethane. Oxidation of octamethylbiphenylene by methanesulfonic acid.* A 1-cm quartz cuvette equipped with a sidearm and Teflon needle valve (Schlenk adapter) was charged with a solution of octamethylbiphenylene (0.12 mM) in anhydrous dichloromethane. Methanesulfonic acid (0.3 ml) was added under an argon atmosphere with the aid of a hypodermic syringe. The color of the solution immediately turned bright blue and the blue solution was analyzed periodically by UV-VIS spectroscopy, as shown in Fig. 1. For example, within 1 min 67% of the  $\text{OMB}^{+\cdot}$  had been formed and essentially no further absorbance change (at  $\lambda_{\text{mon}} = 602$  nm) was observed during the course of next 30 min. The blue solution was quenched by addition of solid sodium carbonate (500 mg) followed by zinc dust (500 mg). The resulting heterogeneous mixture was stirred for 10 min and it was filtered to afford a clear pale yellow solution. The GC and GC-MS analysis of the pale yellow solution (using an internal standard method) showed that octamethylbiphenylene was recovered quantitatively (98.5%). A similar procedure was employed for the oxidation of octamethylbiphenylene using different Brønsted acid in dichloromethane (see the text).

*Protonation and reduction of tetraanisylethylene to its cation-radical.* A dichloromethane solution of tetraanisylethylene (5.04 mM, 0.1 ml) was added to a cooled ( $\approx 0^\circ\text{C}$ ) solution of excess tetrafluoroboric acid (10%, v/v) in dichloromethane (4.9 ml), under an argon atmosphere. The solution immediately turned bright red which upon spectral analysis showed the formation of protonated tetraanisylethylene  $\text{TAE-H}^+$  with the absorption maxima at  $\lambda_{\max} = 508$  nm. The bright red solution remained unchanged for several hours at  $0^\circ\text{C}$ .

It is interesting to note that when an aliquot (0.2 ml)

of the dark red solution was treated with a solution of tetraanisylethylene (5 mg) in dichloromethane (5 ml) under an argon atmosphere, the solution immediately took on a blue coloration which intensified with time (during the course of several hours). The UV-VIS spectral analysis of the highly colored solution showed that the blue color arises due to the formation of  $\text{TAE}^{+\cdot}$  ( $\lambda_{\max} = 565, 926$  nm).

*Oxidation of various electron donors by Brønsted acids in the presence of quinones. General procedure.* A 1-cm quartz cuvette equipped with a sidearm and Teflon needle valve (Schlenk adapter) was charged with tetraanisylethylene (0.4 mM) and chloranil (0.1 mM) in dichloromethane (4.9 ml); methanesulfonic acid (0.1 ml) was added under an argon atmosphere with the aid of a hypodermic syringe. The color of the solution immediately turned blue which further intensified during  $\approx 5$  min period. A quantitative UV-VIS spectral analysis showed that the blue color arises due to the formation of  $\text{TAE}^{+\cdot}$  ( $\lambda_{\max} = 565, 926$  nm) and the yield of the cation radical was estimated to be 98% (based on the extinction coefficient of  $\text{TAE}^{+\cdot}$  cation-radical of  $\epsilon_{926\text{ nm}} = 19\,200\text{ M}^{-1}\text{ cm}^{-1}$ ).<sup>32</sup> Similarly, combinations of other Brønsted acids and quinones (Scheme 1) afforded nearly quantitative yields of  $\text{TAE}^{+\cdot}$ . [Also note that the UV-VIS absorption spectrum of tetraanisylethylene cation-radical ( $\text{TAE}^{+\cdot}$ ) obtained above using various Brønsted acids in the presence of different quinones in Scheme 1 was identical in all respect with those generated using either *orange*  $\text{CRET}^{+\cdot}$  or tris(4-bromophenyl)aminium hexachloroantimonate salts.]

*Spectral measurements.* For the oxidation of the various donors in Table 1, a similar procedure was employed in which a solution of organic donor (0.1–0.2 mM) and chloranil (0.5 mM) in dichloromethane (4.9 ml) was treated with methanesulfonic acid (0.1 ml) and the vivid color changes were monitored by UV-VIS spectroscopy (Figs. 2 and 3). The yields of the cation radicals (based on the amount of added quinone) are listed in Table 1 and were estimated according to the stoichiometry depicted in eqn. (6).

*Isolation of orange  $\text{CRET}^{+\cdot}\text{BF}_4^-$ .* A mixture of 9,10-dimethoxy-1,4:5,8-dimethano-octahydroanthracene ( $\text{CRET}$ ) (270 mg, 1 mmol) and chloranil (296 mg, 1.2 mmol) in anhydrous dichloromethane (10 ml) was stirred, at  $25^\circ\text{C}$  under an argon atmosphere, in a 200-ml flask equipped with a Schlenk adaptor. A solution of  $\text{HBF}_4 \cdot \text{OEt}_2$  (1 ml) in dichloromethane (10 ml) was added with the aid of a hypodermic syringe. The solution immediately turned deep orange-red and the resultant mixture was stirred for 2 h. The highly colored solution was cooled in an ice-salt bath and prechilled ( $\approx 0^\circ\text{C}$ ) anhydrous diethyl ether (100 ml) was added to precipitate the cation radical salt. The orange-red precipitate was filtered under an argon atmosphere and washed thoroughly with anhydrous ether. The crystalline  $\text{CRET}^{+\cdot}\text{BF}_4^-$  salt was

dried at room temperature (25 °C) *in vacuo* to afford fine, orange-red, crystals in excellent yield (310 mg, 87%). The purity of orange  $\text{CRET}^{+\cdot} \text{BF}_4^-$  salts was determined by iodometry<sup>33</sup> as follows. Solutions of  $\text{CRET}^{+\cdot}$  (0.2 mmol, 0.01 M) and tetra-*n*-butylammonium iodide (1 mmol, 0.1 M) in dichloromethane were mixed under an argon atmosphere at 25 °C to afford a dark brown solution. The mixture was stirred for 5 min and titrated (with rapid stirring) by the slow addition of a standard aqueous sodium thiosulfate solution (0.005 M). The purity of  $\text{CRET}^{+\cdot} \text{BF}_4^-$  was found to be greater than 98%.

The ethereal filtrate was washed with water (2 × 25 ml) and dried over anhydrous magnesium sulfate. The analysis of the solution using an internal standard method indicated that the solution contained a mixture of unchanged  $\text{CRET}$  (32 mg, 0.12 mmol), chloranil (186 mg, 0.76 mmol) and hydrochloranil (106 mg, 0.43 mmol). The solvent was evaporated off and the resulting crude mixture was treated with excess acetyl chloride. The usual work-up afforded a solid residue which upon chromatographic separation (using a 1:1 mixture of diethyl ether and hexane as the eluent) yielded hydrochloranil diacetate (120 mg, 0.36 mmol) and the identity of the diacetate was further confirmed by GC and GC-MS comparison with an authentic sample<sup>47</sup> m.p. 251–253 °C (lit.<sup>47</sup> m.p. 252–254 °C).

*General procedures for the catalysis of the benzylic coupling of benzyl alkyl ethers. With orange  $\text{CRET}^{+\cdot}$ .* A catalytic amount of orange  $\text{CRET}^{+\cdot} \text{BF}_4^-$  (36 mg, 0.10 mmol) was added to a cold ( $\approx 0$  °C) solution of benzyl alkyl ether **2** (2.86 g, 10 mmol) in rigorously dried dichloromethane (50 ml) under an argon atmosphere. The solution immediately turned bright yellow and it was stirred for 30 min at 0 °C. The solution was warmed to room temperature, during which time a pinch of zinc dust was added to the yellow-green solution and the mixture was stirred for 5 min. The reaction mixture was filtered and solvent was removed *in vacuo*. Recrystallization of the residue from hexane afforded the diarylmethane **7** as a crystalline solid in excellent yield (1.52 g, 4.8 mmol, 96%); m.p. 147–148 °C (lit.<sup>48</sup> m.p. 147–147.5 °C). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  2.22 (s, 6 H), 3.71 (s, 6 H), 3.80 (s, 6 H), 3.92 (s, 2 H), 6.64 (s, 2 H), 6.71 (s, 2 H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ):  $\delta$  16.12, 29.63, 55.95, 56.13, 105.35, 113.20, 113.80, 124.58, 127.11, 151.17, 151.47. GC-MS: 316,  $M^+$ . 316 calcd. for  $\text{C}_{19}\text{H}_{24}\text{O}_4$ . The other diarylmethanes listed in Table 2 were prepared using the general procedure described above and the spectral data have been described earlier.<sup>25d</sup>

*Tetrafluoroboric acid ( $\text{HBF}_4$ ).* To a prechilled ( $\approx 0$  °C) solution of benzyl methyl ether **1** (224 mg, 1 mmol) in dichloromethane (10 ml) was added a catalytic amount of tetrafluoroboric acid-diethyl ether complex (0.01 ml) under an argon atmosphere. The pale yellow solution was stirred for 50 min and it was quenched with aqueous

sodium bicarbonate (10 ml). The reaction mixture was further diluted with dichloromethane (25 ml) and washed with water (2 × 25 ml), and dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* afforded the pure diarylmethane **7** in quantitative yield. Similarly, the other benzyl alkyl ethers were reacted with catalytic amounts of  $\text{HBF}_4$  and the yields of diarylmethanes thus obtained are compiled in Table 2.

*Nitrosonium tetrafluoroborate ( $\text{NO}^+ \text{BF}_4^-$ ).* A Schlenk flask was charged with nitrosonium tetrafluoroborate (23.4 mg, 0.2 mmol) in a dry box and dichloromethane (50 ml) was added with the aid of a hypodermic syringe. [Note that the  $\text{NO}^+$  salt is insoluble in dichloromethane.] The slurry was cooled in an ice bath (approx. 0 °C) and the benzyl methyl ether **5** (4.48 g, 20 mmol) was added under an argon atmosphere. The reaction mixture slowly turned brown as it was warmed to the room temperature and then stirred for 4 h. Zinc dust was added and the mixture stirred for an additional 5 min. The reaction mixture was filtered under an argon atmosphere and washed with aqueous sodium bicarbonate solution. The dichloromethane layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo* to afford the diarylmethane **10**<sup>25d</sup> as the sole product (3.5 g, 94%).

*Catalysis by the  $\text{HBF}_4$  in the presence of DDQ.* A solution of the benzyl methyl ether **5** (448 mg, 2 mmol) in dichloromethane (20 ml) was cooled in an ice-salt bath and catalytic amounts of tetrafluoroboric acid (0.02 ml) and DDQ (5 mg) were added, under an argon atmosphere. The resulting brown solution was stirred for 3 h, and then quenched with aqueous sodium bicarbonate. The standard work-up as described above yielded an oily residue, which upon GC and GC-MS (internal standard) analysis was shown to consist of the diarylmethane<sup>10</sup> (242 mg, 0.65 mmol, 65%), together with several unidentified products.

*Inhibition of the benzylic coupling of benzyl alkyl ethers. Zinc dust.* A prechilled ( $\approx 0$  °C) dichloromethane solution of orange  $\text{CRET}^{+\cdot}$  (2 ml, 0.01 M) in an ice-salt bath was added to a cold (approx. 0 °C) solution of the benzyl methyl ether **1** (392 mg, 2 mmol) in rigorously dried dichloromethane (20 ml) under an argon atmosphere. The solution immediately turned bright yellow and it was stirred for 2 min at 0 °C. Half of the yellow solution was transferred, with the aid of a cannula, to a prechilled (0 °C) Schlenk flask containing zinc dust, under an argon atmosphere. Both reaction mixtures were stirred for 0.5 h. The control (without zinc dust) was quenched with zinc dust. After being stirred for an additional 2 min both reaction mixtures were individually filtered and the solvent removed *in vacuo*. The residues were analyzed by GC using an internal standard method. Thus, the portion without added zinc showed complete conversion of **1** into the diarylmethane **7** (152 mg, 96%) whereas the portion containing zinc dust showed partial

conversion into **7** (28 mg, 18%) and the remainder (120 mg) of the starting material was recovered.

**Octamethylbiphenylene.** An identical reaction mixture of **1** (20 ml, 2 mmol, 0.1 M) and orange  $\text{CRET}^{+\cdot}$  (0.01 M, 2 ml) in dichloromethane was prepared at 0 °C as described above. After stirring for 2 min, a prechilled ( $\approx 0^\circ\text{C}$ ) solution of octamethylbiphenylene (26.4 mg, 0.1 mmol) in dichloromethane was added. The reaction mixture immediately turned dark blue which upon spectral analysis (UV–VIS) showed the formation of the octamethylbiphenylene radical cation with characteristic absorbances at  $\lambda_{\text{max}} = 602$  nm and 550 nm. The reaction mixture was stirred for an additional 0.5 h, and zinc dust was added. After being stirred for an additional 2 min, the mixture was filtered and the solvent removed *in vacuo* to afford a residue which upon GC-analysis showed only partial conversion into the diarylmethane **7** (80 mg, 25%). The remainder of the starting material and octamethylbiphenylene were recovered unchanged.

**General procedures for the catalytic rearrangement of epoxides and silylated pinacols.** With orange  $\text{CRET}^{+\cdot}$ . A catalytic amount of orange  $\text{CRET}^{+\cdot} \text{BF}_4^-$  (3.6 mg, 0.01 mmol) was added to a cold ( $\approx 0^\circ\text{C}$ ) solution of adamantylideneadamantane oxide **1** (284 mg, 1 mmol) in rigorously dried dichloromethane (10 ml), under an argon atmosphere. The solution immediately took on a bright orange–red coloration, and it was stirred for 2 h at 0 °C. [Since there was no visible color change, the progress of the reaction was monitored by GC and GC–MS analysis by periodically removing an aliquot and by usual work-up by treatment with zinc dust (*vide infra*).] The reaction was warmed to room temperature, during which a pinch of zinc dust was added to the orange–red solution and the mixture was stirred for 5 min. The reaction mixture was filtered and solvent was removed *in vacuo*. Recrystallization of the residue from ethanol afforded the rearranged ketone **10** as a crystalline solid in excellent yield (280 mg, 98%).

The other epoxides in Table 3 were similarly treated in dichloromethane with catalytic amounts of orange  $\text{CRET}^{+\cdot} \text{BF}_4^-$  to afford the corresponding rearranged ketones in excellent yields. The ketones listed in Table 3 were identical with the authentic samples available from a previous study.<sup>19d</sup> The characteristic data are as follows. *Spiro[adamantane-homoadamantanone]* (**10**): m.p. 182–183 °C (lit.<sup>49</sup> m.p. 181–183 °C). *4,4-Bis(4-methoxyphenyl)hexan-3-one* (**11**): oil. IR:  $\nu$  1685  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.68 (t,  $J = 7.2$  Hz, 3 H), 0.88 (t,  $J = 7.2$  Hz, 3 H), 2.31 (m, 4 H), 3.80 (s, 6 H), 6.86 (d,  $J = 8.7$  Hz, 4 H), 7.17 (d,  $J = 8.7$  Hz, 4 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  9.23, 9.57, 30.25, 32.21, 55.23, 65.25, 113.52, 130.48, 133.66, 158.28, 211.91. GC–MS: 312,  $M^+$ , 312 calcd. for  $\text{C}_{20}\text{H}_{24}\text{O}_3$ . *2-Phenyl-2-benzoyladamantane* (**12**): m.p. 135–136 °C (lit.<sup>19d</sup> m.p. 135–136 °C). *2-(4-methoxyphenyl)-2-(4-methoxybenzoyl)adamantane*<sup>19d</sup> (**13**): oil. IR:  $\nu$  1695  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.48–1.63 (m,

7 H), 1.74–1.91 (m, 5 H), 2.94 (s, 2 H), 3.66 (s, 3 H), 3.69 (s, 3 H), 6.59 (d,  $J = 8.7$  Hz, 2 H), 6.80 (d,  $J = 8.7$  Hz, 2 H), 7.42 (sym m, 4 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  26.94, 27.22, 32.90, 33.21, 34.79, 37.62, 55.13, 60.02, 112.82, 113.80, 129.85, 129.97, 132.12, 132.37, 157.95, 161.15, 205.02. GC–MS: 241,  $M^+$ , 241 calcd. for  $\text{C}_{25}\text{H}_{28}\text{O}_3$ . *3,3-Bis(4-methylphenyl)bicyclo[2.2.2]octan-2-one* (**14**). IR:  $\nu$  1684  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.70–1.89 (m, 8 H), 2.31 (s, 6 H), 2.51 (br s, 1 H), 2.98 (br s, 1 H), 7.10 (d,  $J = 8.1$  Hz, 4 H), 7.35 (d,  $J = 8.1$  Hz, 4 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  21.00, 22.60, 23.14, 37.11, 44.24, 61.84, 127.69, 128.90, 135.75, 139.94, 218.00. GC–MS: 304,  $M^+$ , 304 calcd. for  $\text{C}_{22}\text{H}_{24}\text{O}$ . *3,3-Bis(4-methoxyphenyl)bicyclo[2.2.2]octan-2-one* (**15**). IR:  $\nu$  1694  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.68–1.88 (m, 8 H), 2.48 (s, 1 H), 2.89 (s, 1 H), 3.76 (s, 6 H), 6.80 (d,  $J = 8.7$  Hz, 4 H), 7.34 (d,  $J = 8.7$  Hz, 4 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  22.60, 23.11, 37.42, 44.19, 55.27, 61.20, 113.47, 128.90, 135.14, 157.80, 218.41. GC–MS: 336,  $M^+$ , 336 calcd. for  $\text{C}_{22}\text{H}_{24}\text{O}_3$ .  $\alpha,\alpha,\alpha$ -Triphenylacetophenone (*benzopinacolone*, **16**): m.p. 121–122 °C (lit.<sup>25c</sup> m.p. 122 °C).  $\alpha,\alpha,\alpha$ -Tris(4-methylphenyl)-*p*-methylacetophenone (*tolylinacolone*, **17**): m.p. 147–148 °C (lit.<sup>19d</sup> m.p. 146–147 °C).  $\alpha,\alpha,\alpha$ -Tris(4-methoxyphenyl)-*p*-methoxyacetophenone (*anisylpinacolone*, **18**): m.p. 134–136 °C (lit.<sup>19d</sup> m.p. 136–137 °C).

By the use of the general procedure described above various silylated pinacols in Table 4 were transformed into the corresponding pinacolones with catalytic amounts of orange  $\text{CRET}^{+\cdot} \text{BF}_4^-$  in dichloromethane at 0 °C, and the yields of various pinacolones are listed in Table 4. The spectral data for various pinacolones are summarized below. *3,3-Diphenyl-2-butanone* (**6**): m.p. 114–115 °C (lit.<sup>5c</sup> m.p. 112–115 °C). *3,3-Bis(4-methoxyphenyl)-2-butanone* (**8**): m.p. 78–79 °C (lit.<sup>5c</sup> m.p. 79–80 °C). *3,3-Bis(3,4-dimethoxyphenyl)-2-butanone* (**10**): m.p. 51–53 °C. IR:  $\nu$  1702  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.83 (s, 3 H), 2.10 (s, 3 H), 3.78 (s, 6 H), 3.87 (s, 6 H), 6.70–6.84 (m, 6 H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  26.61, 27.31, 55.80, 55.89, 61.47, 110.70, 111.89, 120.52, 135.91, 147.91, 148.57, 209.43. GC–MS: 344,  $M^+$ , 344 calcd. for  $\text{C}_{20}\text{H}_{24}\text{O}_5$ .

**Inhibition of the rearrangement of epoxides and pinacols.** A similar reaction mixture of epoxide **1** (284 mg, 1 mmol) and orange  $\text{CRET}^{+\cdot}$  (3.6 mg, 0.01 mmol) in dichloromethane (10 ml) was stirred at 0 °C for 2 min and a solution of octamethylbiphenylene (26.4 mg, 0.1 mmol) in dichloromethane (2 ml) was added. The solution immediately turned dark blue and the spectral analysis confirmed the formation of octamethylbiphenylene cation-radical ( $\text{OMB}^+$ ). The blue reaction mixture was further stirred for 3 h and was quenched by addition of a pinch of zinc dust. The reaction mixture was stirred for an additional 5 min and then filtered. Evaporation of the solvent *in vacuo* afforded a residue which upon GC-analysis showed only a partial conversion into rearranged ketone **10** (13 mg, 5%) and the remainder of

the starting epoxide **1** was recovered unchanged. Under similar reaction conditions, a mixture of pinacol **1** (386 mg, 1 mmol) and *orange* CRET<sup>+</sup> (3.6 mg, 0.01 mmol) in dichloromethane (10 ml) was quenched with octamethylbiphenylene (26.4 mg, 0.1 mmol) after 2 min. The reaction mixture was further stirred for 2 h and the standard work-up and GC and GC-MS analysis indicated that the mixture consisted of rearranged pinacolone **6** ( $\approx 7\%$ ) and the remainder of the starting silylated pinacol **1** was recovered unchanged. The rearrangement of adamantylideneadamantane oxide **1** and silylated pinacol **1** was similarly inhibited by addition of zinc dust as described above.

*Tetrafluoroboric acid (HBF<sub>4</sub>)*. A prechilled ( $-20^\circ\text{C}$ ) solution of tetraanisylethylene oxide **9** (468 mg, 1 mmol) in dichloromethane (10 ml) was treated with a catalytic amount of tetrafluoroboric acid-diethyl ether complex (0.01 ml), under an argon atmosphere. The solution immediately developed a bright red coloration which changed to pale yellow upon warming to  $0^\circ\text{C}$  [The color changes were monitored by UV-VIS spectroscopy and are presented in Fig. 4.] The pale yellow solution was stirred for 5 min and was quenched with aqueous sodium bicarbonate (10 ml). The reaction mixture was further diluted with dichloromethane (25 ml) and washed with water ( $2 \times 25$  ml), and dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* afforded pure rearranged ketone **18** in quantitative yield. Similarly, the other epoxides and silylated pinacols were reacted with catalytic amounts of HBF<sub>4</sub> and the yields/reaction times for the formation of various rearranged ketones are compiled in Tables 3 and 4, respectively.

*Isomerization of stilbene*. To a prechilled ( $\approx 0^\circ\text{C}$ ) solution of (*Z*)-bis(2,5-dimethoxy-4-methylphenyl)ethylene (328 mg, 1 mmol) in dichloromethane (9 ml) was added a solution of *orange* CRET<sup>+</sup> (1 ml, 1.0 mM) under an argon atmosphere. The solution immediately took on a bright purple coloration. The UV-VIS spectral analysis of the purple solution revealed a well resolved absorption maximum at  $\lambda_{\text{max}} = 502$  nm and a broad band at 595 nm. This absorption spectrum was assigned to the cation-radical of the (*E*)-stilbene derivative. Note that the identical absorption spectrum was obtained by treatment of the (*E*)-stilbene derivative with *orange* CRET<sup>+</sup> in dichloromethane. The highly colored mixture was stirred for 10 min and was quenched with zinc dust. Usual work-up afforded pure (*E*)-stilbene derivative in quantitative yield (320 mg, 98%).

A similar treatment of a solution of (*Z*)-stilbene derivative (328 mg, 1 mmol) in dichloromethane (10 ml) with tetrafluoroboric acid-diethyl ether complex (0.1 ml) at  $0^\circ\text{C}$ , resulted in a pink solution ( $\lambda_{\text{max}} = 487$  nm). The solution was further stirred for 20 min and quenched with aqueous sodium bicarbonate (5 ml). The standard work-up led to a quantitative yield of isomerized (*E*)-stilbene derivative (316 mg, 96%).

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