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Radical−Cation Catalysis in the Synthesis of Diphenylmethanes via the Dealkylative Coupling of Benzylic Ethers

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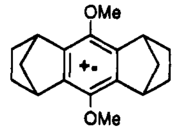
The dealkylative coupling of benzyl alkyl ethers ($ArCH_2OR$) to yield the corresponding diarylmethanes ($ArCH_2Ar$) together with dialkoxymethane ($ROCH_2OR$) is catalyzed by small amounts of 1-electron oxidants (such as aromatic cation radicals, NO^+, *etc.*) or by an equivalent electrochemical (anodic) method. The catalytic method is successfully employed for the facile synthesis of a novel macrocyclic crown ether **18** that contains a diarylmethane linkage. On the basis of the spectral observation of the radical cation $ArCH_2OR^{\bullet+}$ and the excellent catalytic efficiency with turnover numbers in excess of 10^2, an electron-transfer and an alternative electrophilic chain mechanism are discussed for the dealkylative coupling process.

Introduction

Oxidative transformations at the benzylic position of benzyl alkyl ethers have received considerable attention.[1,2] Especially noteworthy are the studies by Weinreb,[3] Schmidt,[4] and co-workers, who utilized electrochemical (anodic) oxidation to unmask the alkyl alcohols from alkyl 4-methoxybenzyl ethers. In contrast, the oxidation of the same alkyl benzyl ethers with quinones[5] such as dicyanodichlorobenzoquinone (DDQ) affords the corresponding esters. Although seemingly disparate, these transformations disclose a common feature in which either a benzylic C−O or C−H bond is initially broken. An alternative, but highly unusual mode of bond breaking in benzyl ethers involves the $Ar-CH_2O$ bond which we recently observed in the unconventional dealkylative nitration of benzyl alkyl ethers ($Ar-CH_2OMe$) to nitroarenes ($Ar-NO_2$) in excellent yields.[6] In the course of these studies, we also discovered a novel catalytic method for the *dealkylative coupling* of benzyl alkyl ethers to the corresponding diphenylmethanes according to the stoichiometry in eq 1. This interesting transformation can be brought about with either catalytic amounts of a mild 1-electron oxidant or by an electrochemical method. We describe in this report how the chemical catalysis of the dealkylative coupling of benzyl alkyl ethers can be most conveniently carried out with small amounts of the highly colored cation radical shown below, which we recently introduced[7] as an excellent 1-electron oxidant.

$$2\,ArCH_2OR \rightarrow ArCH_2Ar + ROCH_2OR \qquad (1)$$



(*Orange* CRET$^{+\bullet}$)

The efficacy of this orange cation radical for electron transfer, hereinafter referred to simply as *Orange* CRET$^{\bullet+}$, is underscored by its reversible reduction potential $E°_{red} = 1.11$ V *vs* SCE. It is readily prepared as the hexachloroantimonate salt which is air stable for prolonged periods, both in solution and in the crystalline state.

Results

I. Catalysis of the Dealkylative Coupling of Benzyl Alkyl Ethers with *Orange* CRET$^{\bullet+}$ in Dichloromethane. When a colorless solution of 0.1 M 4-methyl-2,5-dimethoxybenzyl methyl ether (**1**) in dichloromethane was treated at 0 °C with a small amount (1%) of *Orange* CRET$^{\bullet+}$ under an argon atmosphere, the reaction mixture turned bright yellow immediately. On continued stirring for half an hour, the yellow solution developed a slight green coloration.[8] In a simple workup 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 **8** in excellent yield. On the basis of the amount of added *Orange* CRET$^{\bullet+}$, the yield of diarylmethane **8** was in excess of 10 000%. [Note that the use of the tetrafluoroborate salt of *Orange* CRET$^{\bullet+}$ gave a similar yield of diarylmethane **8**.]

In order to assess the fate of the cleaved group during the dealkylative coupling, the experiment was repeated in deuterated dichloromethane under the same condi-

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[1] (a) Mcdonald, C. E.; Nice, L. E.; Kennedy, K. E. *Tetrahedron Lett.* **1994**, *35*, 57. (b) Xu, Y. C.; Roy, C.; Lebeau, E. *Tetrahedron Lett.* **1993**, *34*, 8189. (c) Horita, K.; Yoshioka, T.; Tanaka, T.; Oikawa, Y.; Yonemitsu, O. *Tetrahedron* **1986**, *42*, 3021. (d) Penn, J. H.; Shu, C.; Deng, D.-L.; Petersen, J. L. *J. Org. Chem.* **1994**, *59*, 3037. (e) Becker, H.; Turner, A. B. In *The Chemistry of Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. II, pp 1351−1355.

[2] (a) Danishefsky, S.; Lee, J. *J. Am. Chem. Soc.* **1989**, *111*, 4829. (b) Lampe, D.; Mills, S.; Potter, B. *J. Chem. Soc., Perkin Trans 1* **1992**, 2899. (c) Schmidt, W.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 802.

[3] Weinreb, S.; Epling, C.; Comi, R.; Reitano, M. *J. Org. Chem.* **1975**, *40*, 1356.

[4] (a) Schmidt, W.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 673. (b) Schmidt, W.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 801.

[5] (a) Dewar, P. S.; Forrester, A. R.; Thomson, R. H. *J. Chem. Soc. (C)* **1971**, 3950. (b) Oikawa, Y.; Horita, K.; Yoshioka, T.; Tanaka, T.; Yonemitsu, O. *Tetrahedron* **1986**, *42*, 3021. (c) Oikawa, Y.; Tanaka, T.; Horita, K.; Yonemitsu, O. *Tetrahedron Lett.* **1984**, *25*, 3841 and references therein.

[6] Rathore, R.; Bosch, E.; Kochi, J. K. *Tetrahedron* **1994**, *50*, 6727.

[7] Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1995**, *60*, 4399. Also see: Rathore, R.; Bosch, E.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1157.

[8] Note that solutions of the parent 2,5-dimethyl-1,4-dimethoxybenzene radical cation[9] in dichloromethane were stable for days at room temperature without apparent decomposition.

[9] See: Hubig, S. M.; Jung, W.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 6233.

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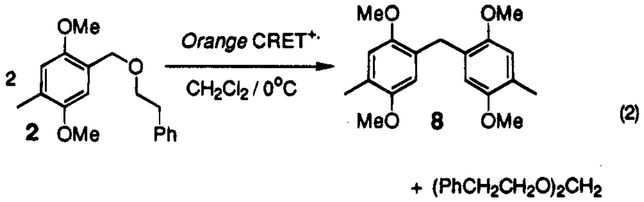
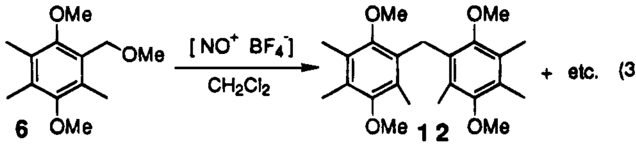
tions. NMR analysis of the dichloromethane solution revealed the presence of diarylmethane **8** and dimethoxymethane, the identities of which were confirmed by spectral comparison of their NMR spectra with those of authentic samples. Owing to the difficulty of precisely assessing the amount of low-boiling dimethoxymethane produced during the dealkylative coupling, the 2-phenethyl ether analogue **2** was also treated with a catalytic amount of *Orange* CRET$^{\bullet+}$ under an argon atmosphere, as described above. The diarylmethane **8** and bis(2-phenylethoxy)methane were isolated in 100 and 85% yields, respectively, according to the stoichiometry in eq 2.[10]



(2)

Application of the same procedure to benzyl alkyl ethers **1**–**5** led to the corresponding diarylmethanes in good to excellent yields, as listed in Table 1. On the other hand, the fully substituted benzyl methyl ether **6** afforded only traces of the corresponding diarylmethane (**12**) even after stirring the reaction mixture for prolonged periods (12 h). Moreover, the relatively less-substituted ether **7** (see Table 1) was found to be similarly unreactive under these conditions (*vide infra*).

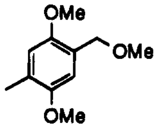
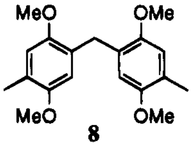
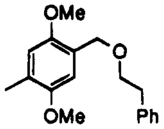
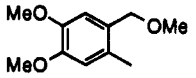
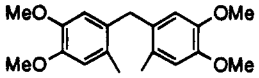
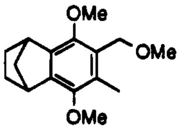
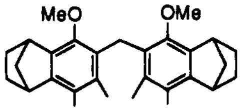
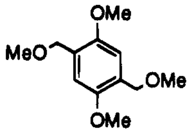
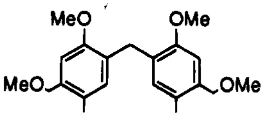
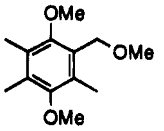
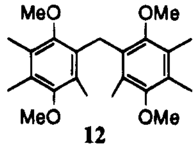
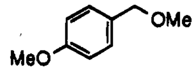
The dealkylative coupling of benzyl alkyl ethers could also be carried out with commercially available 1-electron oxidants, such as the nitrosonium tetrafluoroborate or hexachloroantimonate salts ($NO^+BF_4^-/SbCl_6^-$).[11] For example, the addition of a few crystals of $NO^+BF_4^-$ (~1%) to a dichloromethane solution of **2** (0.1 M) under an argon atmosphere at 0 °C led to the characteristic yellow coloration. Excellent yields of corresponding diarylmethane **8** and bis(2-phenylethoxy)methane were obtained based on the stoichiometry depicted in eq 2. It is noteworthy that benzyl methyl ether **6** when treated with catalytic amounts of $NO^+BF_4^-$ (or $NO^+SbCl_6^-$) salt in anhydrous dichloromethane, furnished the corresponding diarylmethane **12** quantitatively according to eq 3.



(3)

II. Electrocatalysis of the Dealkylative Coupling of Benzyl Alkyl Ethers. The transformation of the benzyl ethers to the corresponding diarylmethanes could also be effected by electrochemical means. Thus, passing a small anodic current at a constant potential of 1.16 V for a short duration through a colorless solution of **2** in dichloromethane (containing a supporting electrolyte) caused the solution to turn bright yellow immediately. Spectrometric analysis of the yellow solution showed a characteristic absorption band with λ_{max} = 460 nm and a shoulder at ~440 nm. Spectral analysis of the anolyte after standing at room temperature for 30 min, followed by a simple nonaqueous workup, showed that the diarylmethane **8** was formed in quantitative yield. The latter corresponded to a yield in excess of 23 150%, on the basis of the amount of current passed through the solution.

Table 1. Catalysis of the Dealkylative Coupling of Benzyl Alkyl Ethers with *Orange* CRET$^{\bullet+}$ in Dichloromethane[a]

	Benzyl Alkyl Ether	Time (h)	Yield[b] (%)	Product
1		0.5 0.4	(96) (95)[c]	 **8**
2		1.0	(97)[d]	"
3		2.0	(96)	 **9**
4		2.5	(87)	 **10**
5		0.5	(44)	 **11**
6		12 4	(<2)[e] (94)[c]	 **12**
7		12	—	d

[a] A 0.1 M solution of benzyl alkyl ether containing 1 mol % *Orange* CRET$^{\bullet+}$ in dichloromethane at 0 °C unless otherwise indicated. [b] Isolated yields. [c] 1 mol % $NO^+BF_4^-$ as the catalyst to replace *Orange* CRET$^{\bullet+}$. [d] Bis(2-phenylethoxy)methane isolated in 82% yield. [e] Starting material recovered.

III. Polymerization of the Bismethoxymethyl Ether 5. The catalytic nature of the coupling procedure prompted us to examine benzylic substrates that could lead to interesting polymeric materials. For example, when a solution of 2,5-bis(methoxymethyl)-1,4-dimethoxybenzene (**5**) in dichloromethane was treated with a catalytic amount of *Orange* CRET$^{\bullet+}$ (2%), the characteristic yellow color was observed immediately. Continuous stirring of the mixture for 2 h led to a voluminous precipitate, which was filtered on a glass frit and dried *in vacuo*. The weight of the dried material accounted for 73% of the material balance. The analysis of the residual dichloromethane solution showed the presence of dimethoxymethane together with reduced (neutral) CRET and traces of diarylmethane **11**. To gain further insight

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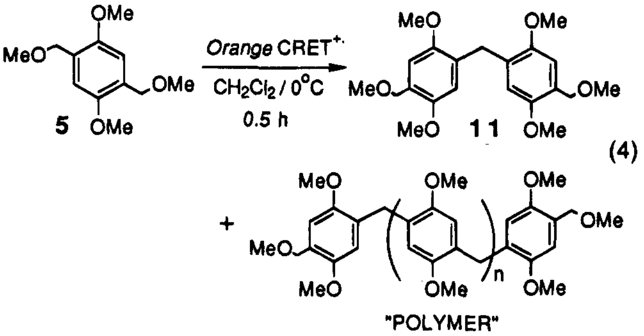
[10] The usefulness of this facile catalytic process for protection and deprotection of alcohols will be described separately.

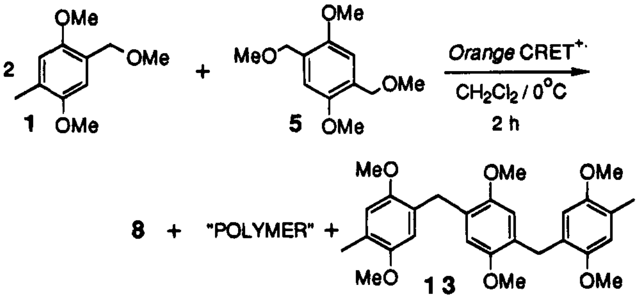
[11] Kim, E. K.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *113*, 4962. Also see: Bandlish, B. K.; Shine, H. J. *J. Org. Chem.* **1977**, *42*, 561.

into the nature of the insoluble product, the same experiment was carried out for a shorter duration (0.5 h) and the polymeric precipitate was recovered by filtration. The filtrate, after removal of solvent *in vacuo* and chromatographic purification, afforded the corresponding diarylmethane **11** in 44% yield (see Table 1) together with unreacted starting material. Although the extreme insolubility of the polymeric precipitate precluded a rigorous analysis, the structure was tentatively assigned to that shown in eq 4 on the basis of degradation studies[12] (see Experimental Section for details).



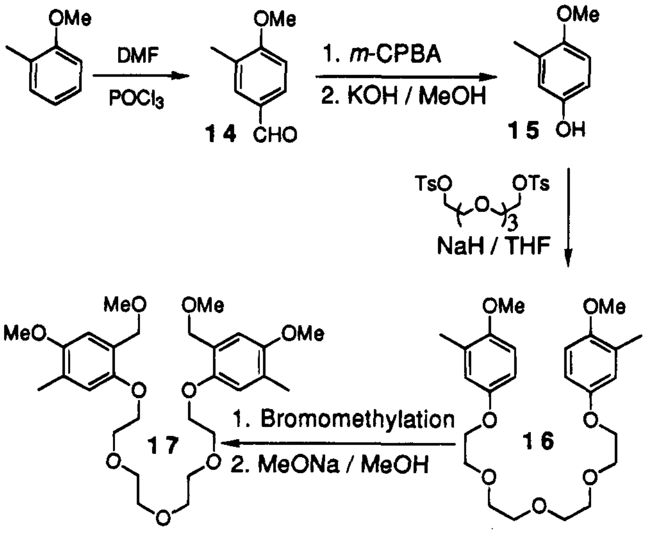
(4)

Since even shortened reaction times still led to a substantial amount of the polymeric material, it was conjectured that the use of a monomethoxymethyl compound **1** as a capping agent for the bis(methoxymethyl) compound **5** might result in more tractable oligomers. Indeed, the treatment of a 2:1 mixture of **1** and **5** in anhydrous dichloromethane with a catalytic amount of *Orange* CRET$^{\bullet+}$, as described above, resulted in the trimeric compound **13** in 30% yield, together with diarylmethane **8** (63%) and a substantial amount of polymeric precipitate.



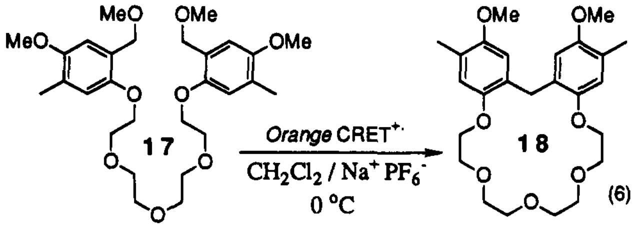
(5)

IV. Macrocyclization of the α,ω-Bis(methoxymethyl)aryl Crown Ether 17 with *Orange* CRET$^{\bullet+}$. Profound Effect of Alkali Metal Cations. The simplicity and efficiency of the catalytic procedure for the formation of diarylmethanes prompted us to explore its synthetic potential in the preparation of macrocyclic crown ethers containing a diarylmethane linkage. Thus, the crown ether **17** with benzyl methyl ether moieties tethered at both ends of a polyethylene glycol chain was prepared as outlined:



Thus, 3-methylanisaldehyde (**14**) readily obtained from *o*-methylanisole via the Vilsmeier−Haack condensation[13] was oxidized with *m*-chloroperbenzoic acid to yield the phenol **15**[14] which was condensed with tetraethylene glycol ditosylate to afford the acyclic ether **16**. Bromomethylation[15] followed by Williamson etherification resulted in the desired crown ether **17** in excellent yield (see Experimental Section).

Treatment of the crown ether **17** (0.1 M) in dichloromethane with a catalytic amount of *Orange* CRET$^{\bullet+}$ immediately resulted in the characteristic yellow color. A gelatinous material separated from the reaction mixture upon stirring for 1 h, and the supernatant dichloromethane layer yielded a viscous residue which contained only small amounts of the cyclized crown **18** (<5%). However, when a similar experiment was conducted in the presence of added sodium hexafluorophosphate (1 equiv), the gelatinous byproduct was not apparent, and a quantitative yield of the cyclized crown **18** was obtained according to the eq 6.



(6)

The potassium salt ($K^+PF_6^-$) was equally effective in promoting this transformation.

V. Aromatic Radical Cation as the Reactive Intermediate in Dealkylative Coupling of Benzyl Alkyl Ethers. The characteristic bright yellow color was observed in all three procedures for catalytic dealkylative coupling of benzyl alkyl ethers to the corresponding diarylmethanes described above, *i.e.* via the addition of *Orange* CRET$^{\bullet+}$ or NO^+ salt or by the electrochemical method. A typical absorption spectrum of the yellow solution, immediately attendant upon the mixing of benzyl ether **1** and *Orange* CRET$^{\bullet+}$ is shown in Figure 1, and it features a well-resolved absorption band with a maximum at λ_{max} = 460 nm and a shoulder at 440 nm. The characteristic twin absorption band was readily assigned to the radical cation of benzyl ether, **1**$^{\bullet+}$, by comparison with the spectrum of the radical cation of the

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[12] Degradation of the polymeric material with iodine monochloride (ICl) to give monomeric chlorinated products is described in the Experimental Section.

[13] Bruce, J. M.; Sutcliffe, F. K. *J. Chem. Soc.* **1956**, 3824.

[14] Godfrey, I. M.; Sargent, M. V.; Elix, J. A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1353.

[15] Bauer, H.; Matz, V.; Krieger, C.; Staab, H. A. *Chem. Ber.* **1994**, *127*, 1993.

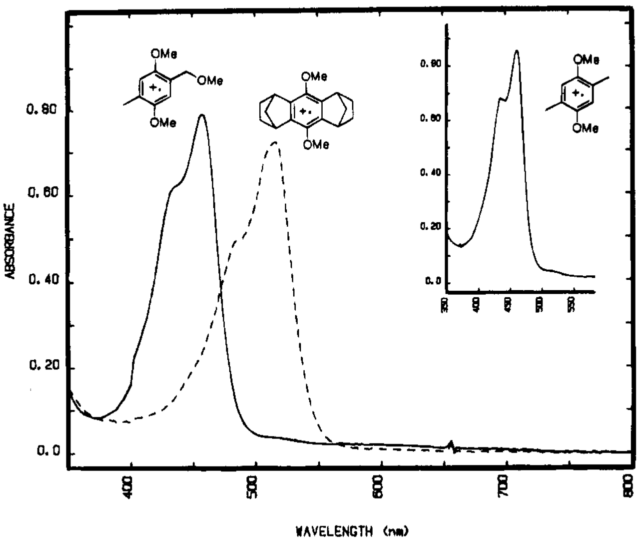
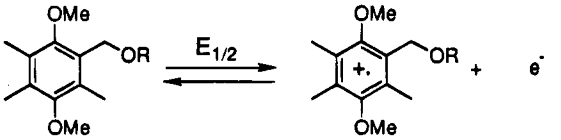


Figure 1. (a) Absorption spectrum (—) taken immediately after mixing prechilled (0 °C) dichloromethane solutions of benzyl methyl ether **1** (0.2 mL, 0.01 M) and *Orange* $CRET^{\bullet+}$ (2 mL, 1.0×10^{-4} M) the absorption spectrum of which is shown as the dashed spectrum. For comparison, the inset presents the absorption spectrum of parent 2,5-dimethyl-1,4-dimethoxybenzene radical cation in dichloromethane.

parent 2,5-dimethyl-1,4-dimethoxybenzene[9] shown in the inset of Figure 1.

We considered the formation of yellow-colored radical cations as an unmistakable visible indicator for the progress of the dealkylative coupling. Since such a reaction intermediate was diagnostic of an electron-detachment pathway, a quantitative examination of the electron-donor properties of the various benzyl alkyl ethers was carried out electrochemically, as follows.

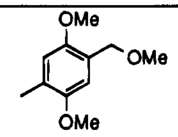
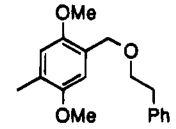
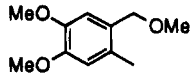
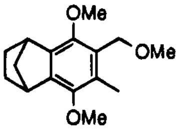
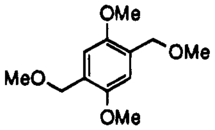
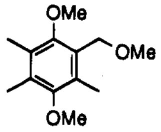
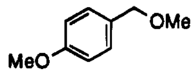
VI. Benzyl Alkyl Ethers as Electron Donors. The various benzyl alkyl ethers in Table 2 were oxidized electrochemically at a platinum electrode in dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Reversible cyclic voltammograms (CV) of the ethers **1**–**5** were consistently obtained at a scan rate $v = 0.1$ V s^{-1}. All voltammograms showed cathodic/anodic peak current ratios of $i_a/i_c = 1.0$ (theoretical) at 25 °C (see Figure 2). The calibration of the CV peaks with ferrocene indicated that the reversible oxidation led to the production of a radical cation via the 1-electron redox couple in eq 7.



(7)

Thus, the benzyl alkyl ethers **1**–**5** in Table 2 were relatively strong electron donors by virtue of their relatively low oxidation potentials ($E_{1/2}$ = ~1.2–1.3 V). In contrast, the benzyl ethers **6** and **7** with anodic peak potentials of 1.51 and 1.63 V, respectively, were relatively poor electron donors and exhibited irreversible cyclic voltammograms. Interestingly, the replacement of a methyl group in parent 2,5-dimethyl-1,4-dimethoxybenzene ($E_{1/2}$ = 1.02 V)[6] by a methoxymethyl group (*i.e.* benzyl ether **1**) increased the oxidation potential of **1** ($E_{1/2}$ = 1.17 V) by 150 mV. Such an increase in the oxidation potential of various ethers relative to that of the parent methyl analogues[6] could be ascribed to the presence of an electronegative oxygen atom at the benzylic position to exert an electron-withdrawing effect.

Table 2. Electrochemical Oxidation Potentials of Various Benzyl Alkyl Ethers[a]

	Benzyl Alkyl Ether	$E_{1/2}$ (V *vs.* SCE)	E_p[b] (V *vs.* SCE)
1		1.17	1.21
2		1.16	1.20
3		1.25	1.30
4		1.24	1.29
5		1.22	1.26
6		c	1.51
7		c	1.63

[a] In anhydrous dichloromethane containing 0.2 M $n\text{-}Bu_4N^+PF_6^-$ at v = 100 mV s^{-1} and 25 °C. [b] Anodic (CV) peak potential. [c] Irreversible cyclic voltammogram at v = 100 mV s^{-1}.

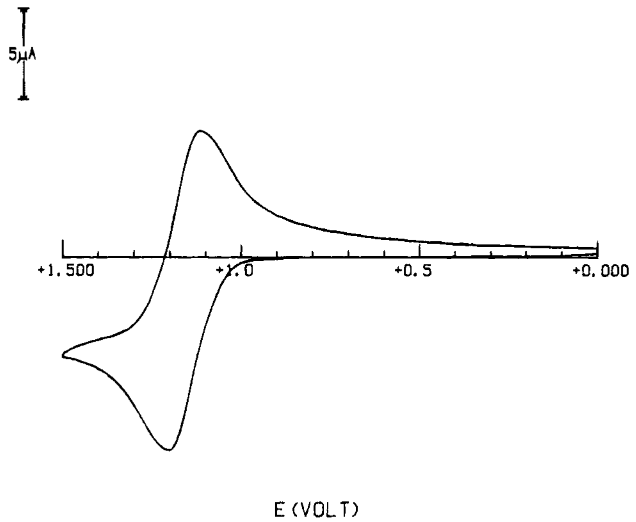


Figure 2. A typical cyclic voltammogram of 5×10^{-3} M 2-[(2-phenylethoxy)methyl]-5-methyl-1,4-dimethoxybenzene (**2**) in anhydrous dichloromethane containing 0.2 M TBAP at a sweep rate of only v = 100 mV s^{-1}.

VII. Inhibition of the Dealkylative Coupling of Benzyl Alkyl Ethers with *Orange* $CRET^{\bullet+}$. In order to clearly establish the role of a radical–cation intermediate in the dealkylative coupling of benzyl alkyl ethers, we attempted to interrupt the catalytic chain process with various quenchers as follows.

Zinc Dust. A prechilled (~0 °C) dichloromethane solution of *Orange* CRET$^{•+}$ was added to a cold solution of benzyl alkyl ether **1** at ~0 °C. The dichloromethane solution, which immediately turned bright yellow, was stirred for 2 min at 0 °C and zinc dust was added. After stirring for 2 min, the reaction mixture was filtered and the solvent removed *in vacuo*. The spectral (NMR) analysis of the residue showed only a partial conversion of **1** to diarylmethane **8** (18%), and the remainder of the starting material was recovered intact.

Octamethylbiphenylene. In a similar experiment, a mixture of **1** and a catalytic amount of *Orange* CRET$^{•+}$ in dichloromethane was prepared at ~0 °C and stirred for 2 min. A solution of octamethylbiphenylene[16] in anhydrous dichloromethane was then added. The solution immediately turned dark blue. Spectral analysis (UV−vis) of the blue solution confirmed the presence of the octamethylbiphenylene radical cation with its characteristic absorption band at λ_{max} = 600 and a shoulder at 550 nm.[11] The reaction mixture was stirred for 0.5 h and zinc dust was added. After stirring for an additional 5 min, the mixture was filtered and the solvent removed *in vacuo* to afford a residue which, on the basis of GC analysis, showed only partial conversion of **1** to diarylmethane **8** (25%). The remainder of the starting material was recovered unchanged.

Tetra-*n*-butylammonium Iodide. The reaction mixture of **1** and a catalytic amount of *Orange* CRET$^{•+}$ in dichloromethane was stirred at 0 °C for 2 min and a solution of tetra-*n*-butylammonium iodide in anhydrous dichloromethane (2 mL) was added under an argon atmosphere. The solution which turned immediately pale brown, was stirred for 0.5 h. Evaporation of the solvent *in vacuo* afforded a residue that showed only a partial conversion of **1** to diarylmethane **8** (25%). The remainder of the starting material was recovered unchanged.

VIII. Effect of the Solvent and Acids on Dealkylative Coupling. The catalytic efficiency of the dealkylative coupling according to the stoichiometry in eq 1 was examined in several selected solvents with **1** as the prototypical benzyl methyl ether. The results in Table 3 (entries 1 and 2) indicate that *Orange* CRET$^{•+}$ catalyzed the formation of diarylmethane **8** in anhydrous acetonitrile as effectively as that carried out in dichloromethane (compare entry 1 in Table 1). Importantly, the presence of 1% v water (to approximate wet acetonitrile) had only a minor retarding effect (entry 3). On the other hand, the use of protic solvents such as methanol (entry 4) and basic solvents such as pyridine (entry 5) led to significantly lower yields of diarylmethane **8**, under otherwise the same reaction conditions.[17]

The dealkylative coupling of benzyl methyl ether **1** in anhydrous acetonitrile was also promoted by 1 mol % fluoroboric or trifluoromethanesulfonic acid (see Table 3, entries 6 and 7), but not by hydrogen bromide (entry 8). However, the acid-catalyzed dealkylative coupling of **1** was ineffective when it was carried out in wet acetonitrile (entries 11 and 12).

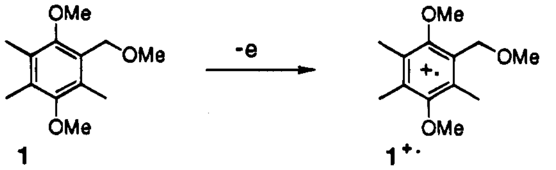
Table 3. Effect of the Medium and Acids on the Dealkylative Coupling of Benzyl Methyl Ether 1[a]

solvent	additive	time (h)	yield (%)[b]
acetonitrile[c]	none	0.75	98 (<1)
acetonitrile[c,e]	none	0.18	98 (<1)
acetonitrile (wet)[d,e]	none	0.18	67 (30)
methanol	none	0.50	<1 (95)
pyridine	none	0.50	<1 (98)
acetonitrile[c]	HBF_4[f]	0.75	72 (25)
acetonitrile[c]	CF_3SO_3H[f]	0.75	78 (20)
acetonitrile[c]	HBr[g]	0.75	0 (94)
acetonitrile[c]	HBr[h]	0.75	0 (*k*)
acetonitrile[c]	HBF_4[i]	0.18	97 (<1)
acetonitrile (wet)[d]	HBF_4[i]	0.18	20 (77)
acetonitrile (wet)[j]	HBF_4[i]	0.18	0 (97)

[a] In 0.1 M solution of benzyl methyl ether 1 with 1 mol % *Orange* CRET$^{•+}$ added at 0 °C, unless indicated otherwise. [b] Diarylmethane **8** isolated. Recovered **1** in parentheses analyzed by GC−MS (internal standard). [c] Anhydrous (see Experimental Section). [d] Anhydrous acetonitrile containing 1% v water. [e] 4 mol % *Orange* CRET$^{•+}$ added. [f] 1 mol %. [g] 2 mol %. [h] Saturated with anhydrous HBr. [i] 4 mol %. [j] Anhydrous acetonitrile containing 5% v water. [k] Bromo derivative formed; see Experimental Section.

Discussion

Treatment of benzyl alkyl ethers **1−5** with a catalytic amount (1%) of radical cation salt (*Orange* CRET$^{•+}$) in dichloromethane readily leads to the corresponding diarylmethanes in excellent yields according to the stoichiometry depicted in eqs 1 and 2. The mild reaction conditions coupled with a simple nonaqueous work-up procedure makes this coupling reaction an ideal method for the construction of diarylmethane linkages. Furthermore, the high catalytic efficiency of the dealkylative coupling, with turnover numbers in excess of 10^2, also allows for an alternative electrochemical procedure. Indeed, the facile chemical promotion with small amounts of radical cations[18] and anodic promotion with limited Coulombs both point to a chain process for the dealkylative coupling that is initiated by oxidation. This formulation is supported by the rapid appearance of the radical cation $1^{•+}$ (see Figure 1) immediately upon either (a) the introduction of *Orange* CRET$^{•+}$ or (b) the passage of a small anodic current through the solution of benzyl alkyl ether **1**, *i.e.*



1 $\quad$ $\mathbf{1}^{+\cdot}$ (8)

Moreover, the critical role of radical−cation intermediates and the radical-chain character is demonstrated by the effective inhibition of the dealkylative coupling by the addition of minor amounts of such diverse reducing agents as zinc dust, octamethylbiphenylene, and iodide (as the tetra-*n*-butylammonium salt). In each case, inhibition is visually and spectrally characterized by the immediate disappearance of the yellow color of the cation radical $1^{•+}$ with its characteristic absorption band at λ_{max} = 460 nm (Figure 1). Electron transfer as described in eq 9 is directly related to the efficacy of the electron-rich aromatic quencher octamethylbiphenylene (OMB) with E°_{ox} = 0.80 V *vs* SCE, since the disappearance of the

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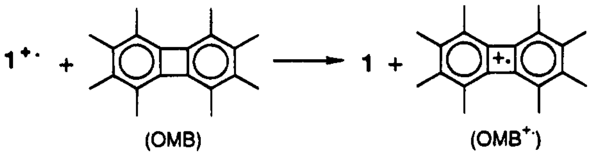
[16] Hart, H.; Teuerstein, A. *Synthesis* **1979**, 693.

[17] Control experiments demonstrated that the radical cation $1^{•+}$ persisted for prolonged periods in acetonitrile (somewhat less in wet acetonitrile), but it was extremely short-lived (<1 s) in either methanol or pyridine (see Experimental Section).

[18] Similar yields of diarylmethanes were obtained with tris(*p*-bromophenyl)aminium hexachloroantimonate ("magic blue") as the 1-electron oxidant.

yellow color of $1^{\bullet+}$ is simultaneously accompanied by the appearance of the dark blue color of the radical cation $OMB^{\bullet+}$ with λ_{max} = 600 (550 sh) nm,[11] *i.e.*



(9)

Radical cations as readily visible intermediates provide the key to understanding the role of catalysts in dealkylative coupling. Thus the coupling efficiency depends on the ability of a catalyst such as *Orange* $CRET^{\bullet+}$ to effect an initial electron transfer from the benzyl ether, *i.e.*

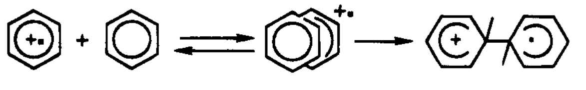
$$ArCH_2OR + \underset{\substack{(Orange)\\ \lambda_{max}\ 518\ nm}}{CRET^{\bullet+}} \rightarrow \underset{\substack{(Yellow)\\ \lambda_{max}\ 460\ nm}}{ArCH_2OR^{\bullet+}} + CRET \qquad (10)$$

The various benzyl alkyl ethers can be divided into two groups on the basis of the 1-electron oxidation potentials in Table 2. Thus, the first group of ethers **1-5** consists of relatively strong electron donors by virtue of their low oxidation potentials ($E_{1/2}$ = 1.15–1.30 V *vs* SCE). It follows that the free energy change ΔG_{et} for the electron transfer in eq 10, based on the reduction potential of *Orange* $CRET^{\bullet+}$ ($E°_{red}$ = 1.11 V *vs* SCE),[7] are all exergonic, and electron-transfer rates are expected to be fast. Indeed, the benzyl alkyl ethers **1-5** react smoothly in the presence of catalytic amounts of *Orange* $CRET^{\bullet+}$ to afford the corresponding diarylmethanes in high yields (see Table 1). Contrastingly, the second group of benzylic ethers (**6** and **7**) have oxidation potentials which are substantially more positive (E_p = 1.51 and 1.63 V, respectively), and they are essentially unreactive under similar reaction conditions.[19] However, the use of the stronger 1-electron oxidant nitrosonium (NO^+ with $E°_{red}$ = 1.50 V)[20] promotes the dealkylative coupling of benzyl alkyl ether to the diarylmethane **12** in quantitative yield (see eq 3). Such a facile promotion is consistent with the favorable free energy change required for efficient electron transfer in eq 11.[21]

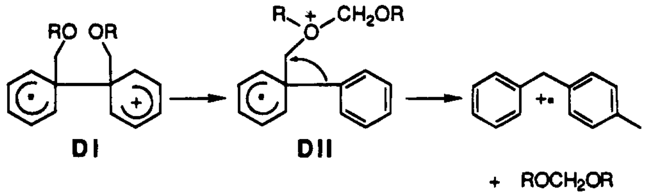
$$\mathbf{6} + NO^+ \xrightarrow{\Delta G_{et}} \mathbf{6}^{\bullet+} + NO \qquad (11)$$

Faced with the compelling evidence for aromatic radical cations as intermediates in a highly efficient chain process, let us formulate a sequence of discrete steps by which a pair of benzyl ethers ($ArCH_2OR$) are converted to the corresponding diarylmethane ($ArCH_2Ar$). Such a formulation must be highly unusual insofar as it requires the rapid scission of an usually unreactive $Ar-CH_2OR$ bond in order to produce the byproduct $ROCH_2OR$ in eq 1 (especially under the very mild conditions under which it takes place[22]). Basically, there are two different types of chain processes which could accommodate aromatic radical cations in such a labilization of $Ar-CH_2OR$. In the direct mechanism, aromatic radical cations are critical intermediates in the catalytic cycle; and it is thus designated as *electron-transfer catalysis*. In the alternative mechanism, the aromatic radical cation is an indirect participant in the catalytic cycle—merely serving as the precursor to the active benzylic cation (or its functional equivalent) in *electrophilic catalysis*. The salient features of the direct and indirect participation of aromatic radical cations in electron-transfer and electrophilic catalysis, respectively, are identified as follows.

A. Electron-Transfer Catalysis of Dealkylative Coupling. Aromatic radical cations as electron-deficient species are known to readily associate with their uncharged counterparts and lead to the distonic dimeric cation radical,[23] *e.g.*


(12)

As applied to benzyl ethers, the facile self-association of aromatic nuclei in eq 12 would lead to distonic σ-adducts (**DI**) that contain labile CH_2OR groups in allylic positions, *i.e.*



(13)

According to eq 13, the distonic adduct **DI** can undergo rearomatization via an intramolecular transfer of CH_2OR to form the aromatic adduct **DII**. The ready loss of dialkoxymethane from **DII** is facilitated via anchimeric assistance of the neighboring aromatic group (reminiscent of 1,2-aryl shifts in related Wagner–Meerwein rearrangements).[26] As such, the exergonic driving force for the rearrangement is derived from the formation of the stabilized diarylmethane radical cation ($\mathbf{8}^{\bullet+}$).[27] It is important to emphasize that the mechanistic pathway

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[19] It could be readily shown (by the absence of any color change) that benzyl ethers **6** and **7** did not undergo electron transfer to *Orange* $CRET^{\bullet+}$.

[20] Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1990**, *29*, 4196.

[21] The values of ΔG_{et} for **6** and **7** with NO^+ is calculated to be only 0.23 and 3.0 kcal mol^{-1} based on the values of $E°_{ox}$ in Table 1.

[22] The cleavage of such Ar–C bonds (*e.g.*, in the rearrangement and disproportionation of polyalkylbenzenes in the Jacobsen reaction) requires strong Lewis acid catalysts and is usually carried out at elevated temperatures. See: March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; pp 565.

[23] (a) The cationic π-dimer in eq 12 has been examined extensively by Brocklehurst, Lau, and co-workers.[24] (b) The distonic radical–cation adduct has ample literature precedent in the synthesis of a variety of biaryls.[25]

[24] (a) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2582; 2588. (b) Lau, W.; Kochi, J. K. *J. Org. Chem.* **1986**, *51*, 1801.

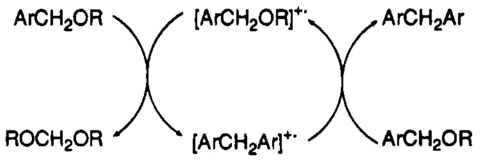
[25] (a) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55 and references therein. (b) Also see: Kerr, J. B.; Jempty, T. C.; Miller, L. *J. Am. Chem. Soc.* **1979**, *101*, 7338 and references therein.

[26] For the concertedness (and phenonium ion intermediates) of neighboring aryl rearrangements with the loss of the (ethereal) leaving group, compare with: (a) Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. In *Carbonium Ions*; Olah, G. A.; Schleyer, P., Eds.; Wiley: New York, 1972; Vol. 3, pp 1347 ff. (b) Wheland, G. W. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1960; pp 596–604. (c) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 1151 ff.

[27] The driving force of 1.6 kcal mol^{-1} for the rearrangement in eq 13 can be approximated as the potential difference for the formation of $\mathbf{8}^{\bullet+}$ ($E_{1/2}$ = 1.10 V)[28] and $\mathbf{1}^{\bullet+}$ ($E_{1/2}$ = 1.17 V) in dichloromethane.

[28] Rathore, R. Unpublished results.

Scheme 1



presented in eq 13 is critically dependent on the coupling of aromatic nuclei via the pathway outlined in eq 12. It is then particularly illuminative that the forced juxtaposition of two aromatic rings via the tethered crown ether (ligand) leads to high coupling yields when it is carried out in the presence of alkali metal ions (Na^+ and K^+) in eq 6. In other words, we believe that the flexibility of the polyether chain in crown ether **17** does not allow the two aromatic rings to be optimally arranged for the cyclization reaction. Instead, a linear polymerization at both ends of **17** is favored to form the gelatinous byproduct of eq 6 (see the Experimental Section). However, the binding of the alkali metal ion to the polyether (ligand) chain can cause a conformational change that allows the two aromatic rings in **17** to be in close proximity for coupling and thus yield the cyclized crown **18** in high yields.[29] Although each of the discrete steps in eq 13 is mechanistically reasonable, they follow the rate-limiting electron-transfer step in eq 10. As such, they are extremely difficult to verify experimentally with independent supporting evidence.[30] Nonetheless, eq 13 provides the reasonable prediction that the radical cations $ArCH_2OR^{\bullet+}$ and $ArCH_2Ar^{\bullet+}$ are the reactive intermediates in a highly efficient electron-transfer chain (ETC) process, as depicted in Scheme 1. The propagation sequence in Scheme 1 emphasizes the critical role of electron-transfer in the catalytic transformation of the benzyl ethers.

B. Electrophilic Catalysis of Dealkylative Coupling. Benzylic cations serve as conventional electrophiles in aromatic substitution to produce various diarylmethanes, *e.g.*[31]

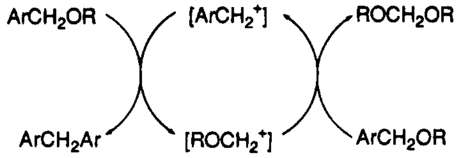
$$ArCH_2^+ + Ar'H \rightarrow ArCH_2Ar' + H^+ \qquad (14)$$

Such an electrophilic aromatic substitution as applied to the dealkylative coupling of benzyl alkyl ethers would lead to the displacement of the alkoxymethyl cation,[32] *i.e.*

$$ArCH_2^+ + ArCH_2OR \rightarrow ArCH_2Ar + ROCH_2^+ \qquad (15)$$

which upon its facile coordination[33] onto the ethereal oxygen of $ArCH_2OR$ would result in the catalytic cycle depicted in Scheme 2.[34] The propagation sequence for electrophilic catalysis in Scheme 2 emphasizes the critical role of the carbocations $ArCH_2^+$ and $ROCH_2^+$ in the chain transformation of benzyl ethers.[35] As such, the aromatic radical cation serves an indirect role in merely providing a source of the active benzylic cation, either by mesolytic scission,[36] *i.e.*

Scheme 2



$$ArCH_2OR^{\bullet+} \rightarrow RO^{\bullet} + ArCH_2^+ \qquad (16)$$

or via deprotonation/acidolysis,[37] *i.e.*

$$ArCH_2OR^{\bullet+} \rightarrow (ArCHOR^{\bullet}) + H^+ \xrightarrow{ArCH_2OR} ROH + ArCH_2^+ \qquad (17)$$

Since the interconversion of $ArCH_2^+$ and $ROCH_2^+$ in Scheme 2 is akin to the well-known interconversion of benzylic cations and protons in the acid-catalyzed condensation of benzylic alcohols to various diarylmethanes,[38] electrophilic catalysis represents a more or less conventional mechanism for the dealkylative dimerization of benzyl alkyl ethers in eq 1.

Mechanistic Ambiguity in Electron-Transfer Catalysis *vs* Electrophilic Catalysis. The catalytic cycles for the dealkylative coupling of benzyl alkyl ethers as presented in Schemes 1 and 2 underscore the more general problem of delineating electron-transfer from electrophilic pathways in a variety of other transformations.[39] Experimentally, the problem resolves into distinguishing the chemical behavior of paramagnetic radical cations from that of diamagnetic cations as *reactive* intermediates. As applied to the transient intermediates pertinent to the dealkylative coupling of benzyl ethers, we may rely on a weak base such as acetonitrile to distinguish between $ArCH_2OR^{\bullet+}$ and $ArCH_2^+$. Since the latter is a highly (coordinatively) unsaturated species, it (like $ROCH_2^+$) is more likely than $ArCH_2OR^{\bullet+}$ to be trapped by this medium (*i.e.* wet acetonitrile used in the Ritter reaction).[40] On the other hand, the aromatic radical cation is a rather persistent species in wet

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[29] For example, see: Pierre, J.-L. *Tetrahedron Lett.* **1988**, 933 and references therein.

[30] As a type of Wagner−Meerwein rearrangement is concerned, the 1,2-aryl shift in eq 13 is unique in that the cationic product is a paramagnetic *radical* cation.

[31] (a) Yoshida, K. *Electrooxidation in Organic Chemistry. The Role of Cation Radicals as Synthetic Intermediates*; Wiley: New York, 1984; pp 130 ff. (b) Bosch, E.; Kochi, J. K. *J. Org. Chem.* **1994**, *59*, 3314. (c) White, E. H.; DePinto, J. T.; Polito, A. J.; Bauer, I.; Roswell, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 3708. (d) Welch, C. M.; Smith, H. A. *J. Am. Chem. Soc.* **1951**, *73*, 4391.

[32] Olah, G. A; Svoboda, J. J. *Synthesis* **1973**, 52. See also: Streitwieser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962; p 103.

[33] For the facile formation of trialkyloxonium ions, see: Perst, H. *Oxonium Ions in Organic Chemistry*; Academic Press: New York, 1971.

[34] We thank a referee for kindly pointing out this possibility.

[35] Benzylic and alkoxymethyl cations that are coordinated to ethers could also be the reactive intermediates in Scheme 2.

[36] For the mesolytic cleavage of C−C bonds in cation radicals, see: Maslak, P.; Narvaez, J. N. *Angew. Chem.* **1990**, *102*, 302. As yet, there is no documented example of the mesolytic cleavage of an ether radical cation as in eq 16. [However, see Fasani et al. in ref 37c.]

[37] For the facile loss of (benzylic) protons from related radical cations in the first step of eq 17, see: (a) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472. (b) Masnovi, J. M.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2263. (c) Fasani, E.; Mella, M.; Albini, A. *J. Chem. Soc., Perkin Trans 2* **1995**, 449. (d) Lewis, F. D.; Petisce, J. R. *Tetrahedron* **1986**, *42*, 6207. (e) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

[38] (a) Simons, J. H.; Archer, S. *J. Am. Chem. Soc.* **1940**, *62*, 1623. (b) McKenna, J. F.; Sowa, F. J. *J. Am. Chem. Soc.* **1937**, *59*, 470 and references therein.

[39] (a) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993. (b) Yueh, W.; Bauld, N. L. *J. Chem. Soc., Perkin Trans 2* **1995**, 871. (c) Ciminale, F.; Lopez, L.; Mele, G. *Tetrahedron* **1994**, *50*, 12685. (d) Lopez, L.; Troisi, L. *Tetrahedron Lett.* **1989**, *30*, 3097. (e) Bauld, N. L.; Bellville, D. J.; Harirchian, B.; Lorenz, K. T.; Pabon, P. A., Jr.; Reynolds, D. W.; Wirth, D. D.; Chiou, H. S.; Marsh, B. K. *Acc. Chem. Res.* **1987**, *20*, 371. (f) Chanon, M. *Bull. Soc. Chim. Fr.* **1985**, 209. (g) Bockman, T. M.; Kochi, J. K. *J. Phys. Org. Chem.* **1994**, *7*, 325.

acetonitrile.[17] Thus the efficient conversion of benzyl methyl ether **1** by *Orange* CRET$^{\bullet+}$, but not by acids, in Table 3 (entries 3 and 11) points to electron-transfer catalysis as the favored pathway for dealkylative coupling. We hasten to add, however, that the mechanistic distinction is not completely rigorous since a slight change in the water content in wet acetonitrile is sufficient to blur the change in catalytic efficiency (compare entries 2 and 3 with entry 11 in Table 3).

Summary and Conclusions

A highly efficient catalytic procedure is described for the dealkylative coupling of benzyl alkyl ethers to the corresponding diarylmethanes which can be initiated either with small amounts of 1-electron oxidant (*e.g. Orange* CRET$^{\bullet+}$ and NO$^+$) or by an equivalent electrochemical (anodic) method. The synthetic potential of the method is demonstrated in the facile preparation of a macrocyclic crown ether **18** via the alkali metal ion-assisted cyclization in eq 6. The critical role of radical cations as viable intermediates and the radical-chain character is demonstrated by the effective inhibition of the dealkylative coupling process by various types of 1-electron reducing agents. On the basis of these observations and the high catalytic efficiency of the coupling reaction (even in wet acetonitrile), the electron-transfer chain (ETC) mechanism in Scheme 1 is favored over the alternative electrophilic mechanism in Scheme 2. We hope that further studies will provide a more definitive basis for the mechanistic distinction.[41]

Experimental Section

Materials. 2-Methyl-1,4-dimethoxybenzene, 2,5-dimethyl-1,4-dimethoxybenzene, 4-methyl-1,2-dimethoxybenzene,[42] 2,3,5-trimethyl-1,4-dimethoxybenzene, and 5,8-dimethoxy-6-methyl-1,4-methano-1,2,3,4-tetrahydronaphthalene were available from the literature procedures.[6] The radical–cation *Orange* CRET$^{\bullet+}$ was readily isolated as the stable hexachloroantimonate ($SbCl_6^-$) and tetrafluoroborate (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 antimony pentachloride ($SbCl_5$) and nitrosonium tetrafluoroborate, respectively.[7] CRET (precursor for *Orange* CRET$^{\bullet+}$) can be easily prepared in multigram quantities from the corresponding bis-annulated hydroquinone which was easily obtained by the Diels–Alder condensation of *p*-benzoquinone with cyclopentadiene followed by hydrogenation over palladium/carbon and aromatization with bromine in excellent yield. Nitrosonium tetrafluoroborate (Strem) was stored in a Vacuum Atmospheres HE-493 dry box kept free of oxygen. Tetra-*n*-butylammonium hexafluorophosphate, tetra-*n*-butylammonium iodide, 1,4-dimethoxybenzene, 2-methylanisole, and tetraethylene glycol ditosylate were commercially available (Aldrich) and used as received. Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (~20% by volume) until the acid layer remained clear. 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. Acetonitrile (Fischer) was stirred with $KMnO_4$ for 24 h, and the mixture was refluxed until the liquid was colorless. The MnO_2 was removed by filtration. The acetonitrile was distilled from P_2O_5 under an argon atmosphere and then refluxed over CaH_2 for 6 h. After distillation from the CaH_2, the acetonitrile was stored in a Schlenk flask under an argon atmosphere.

Synthesis of Benzyl Alkyl Ethers. The benzyl alkyl ethers used in this study were prepared by Williamson method using sodium alkoxides and benzyl halides obtained from the corresponding arenes using halomethylation reaction,[6,15] unless otherwise specified.

General Procedure. A solution of 2-(bromomethyl)-5-methyl-1,4-dimethoxybenzene[43] (4.9 g, 20 mmol) in minimum amount of methanol (25 mL) was added to a freshly prepared solution of sodium methoxide (2.3 g sodium in 50 mL methanol) at 0 °C. The mixture was stirred at room temperature for 2 h, diluted with water (200 mL), and extracted with ether (3 × 50 mL). The ether extracts were washed with water (2 × 50 mL) and saturated brine and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo*, and the syrup thus obtained was purified by column chromatography using hexane and ether mixture (8:2) as eluant to afford pure benzyl methyl ether **1** (3.76 g, 96%). Characteristic spectral data for various benzyl alkyl ethers are given below:

2-(Methoxymethyl)-5-methyl-1,4-dimethoxybenzene (1): oil; ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 3H), 3.41 (s, 3H), 3.76 (s, 3H), 3.79 (s, 3H), 4.47 (s, 2H), 6.69 (s, 1H), 6.88 (s, 1H); ^{13}C NMR ($CDCl_3$) 15.94, 55.51, 55.68, 57.85, 69.03, 111.06, 113.44, 124.02, 126.05, 150.47, 151.37; GC–MS 196, M$^+$, 196 calcd for $C_{11}H_{16}O_3$.

2-[(2-Phenylethoxy)methyl]-5-methyl-1,4-dimethoxybenzene (2): mp 46–47 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H), 3.08 (t, 2H), 3.84 (s, 3H), 3.85 (s, 3H), 3.86 (t, 2H), 4.71 (s, 2H), 6.80 (s, 1H), 6.98 (s, 1H), 7.28–7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) 16.09, 36.23, 55.57, 55.79, 67.16, 71.12, 110.86, 113.53, 124.45, 125.88, 128.08, 128.79, 139.05, 150.38, 151.51; GC–MS 286, M$^+$, 286 calcd for $C_{18}H_{22}O_3$.

4-(Methoxymethyl)-5-methyl-1,2-dimethoxybenzene (3): oil; ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3H), 3.43 (s, 3H), 3.87 (s, 3H), 3.89 (s, 3H), 4.41 (s, 2H), 6.73 (s, 1H), 6.92 (s, 1H); ^{13}C NMR ($CDCl_3$) 17.44, 55.07, 55.16, 57.24, 71.89, 111.62, 112.87, 127.46, 128.03, 146.06, 147.47; GC–MS 196, M$^+$, 196 calcd for $C_{11}H_{16}O_3$.

5,8-Dimethoxy-6-(methoxymethyl)-7-methyl-1,4-methano-1,2,3,4-tetrahydronaphthalene (4):[6] oil; ^{1}H NMR ($CDCl_3$) δ 1.23 (sym m, 2), 1.46 (sym m, 1), 1.67 (sym m, 1), 1.92 (sym m, 2), 2.25 (s, 3), 3.40 (s, 3), 3.57 (br s, 2), 3.74 (s, 3), 3.80 (s, 3), 4.43 (AB pattern, $\Delta\nu_{AB}$ = 21.06 Hz, J_{AB} = 9.9 Hz, 2H, $-CH_2-$ of methoxymethyl group); ^{13}C NMR ($CDCl_3$) δ 11.52, 26.84, 40.55, 40.60, 48.60, 58.05, 60.60, 61.80, 66.29, 126.77, 129.16, 137.36, 140.59, 148.00, 148.57; GC–MS 262, M$^+$, 262 calcd for $C_{16}H_{22}O_3$.

2,5-Bis(methoxymethyl)-1,4-dimethoxybenzene (5): mp 57–58 °C (lit.[44] mp 56–59 °C); ^{1}H NMR ($CDCl_3$) δ 3.39 (s, 6), 3.77 (s, 6), 4.46 (s, 4), 6.90 (s, 2); ^{13}C NMR ($CDCl_3$) δ 55.84, 58.19, 69.11, 111.16, 126.10, 150.73; GC–MS 226, M$^+$, 226 calcd for $C_{12}H_{18}O_4$.

2-(Methoxymethyl)-3,5,6-trimethyl-1,4-dimethoxybenzene (6):[6] mp 35–36 °C; ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3), 2.19 (s, 3), 2.30 (s, 3), 3.42 (s, 3), 3.64 (s, 3), 3.69 (s, 3), 4.47 (s, 2); ^{13}C NMR ($CDCl_3$) δ 11.63, 12.42, 12.71, 58.05, 59.88, 61.73, 66.69, 127.31, 127.83, 129.12, 130.91, 152.94, 153.50; GC–MS 222, M$^+$, 224 calcd for $C_{13}H_{20}O_3$.

4-Methoxymethylanisole (7): oil; ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 3H), 3.74 (s, 3H0, 4.37 (s, 2H), 6.87 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) 54.74, 57.35, 73.95, 113.39, 128.99, 129.97, 158.89; GC–MS 152, M$^+$ 1152 calcd for $C_9H_{12}O_2$.

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[40] Wet acetonitrile is more effective in trapping carbocations (in the Ritter reaction), probably owing to the reversibility in the formation of the nitrilium adduct. For example, see: Krimen, L. K.; Cota, D. J. *Org. React.* **1969**, *17*, 213.

[41] For example, Scheme 1 predicts the dialkoxymethane ($ROCH_2OR$) to be wholly derived from $ArCH_2OR$, whereas Scheme 2 predicts an unsymmetrical dialkoxymethane ($ROCH_2OS$) to be formed in an alcoholic solvent (SOH). If an alcohol could be found in which aromatic radical cations such as $1^{\bullet+}$ can persist,[17] it could serve to distinguish electron transfer from electrophilic catalysis.

[42] Flack, J. R.; Miller, L. L.; Stermitz, F. R. *J. Am. Chem. Soc.* **1974**, *96*, 2981.

[43] Staab, H. A.; Haffner, H. *Chem. Ber.* **1977**, *110*, 3358.

[44] Schill, G. *Justus Liebigs Ann. Chem.* **1966**, *691*, 79.

Instrumentation. The UV–vis absorption spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer. The ^{1}H 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 a HP 5970 mass spectrometer (EI, 70 eV).

Cyclic Voltammetry of Benzyl Alkyl Ethers. 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 (~1 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 gauze that was separated from the working electrode by ~3 mm. The CV measurements were carried out in a solution of 0.2 M supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate) and 5×10^{-3} M benzyl alkyl ether in dry dichloromethane under an argon atmosphere. All the cyclic voltammograms were recorded at the sweep rate of 100 mV s^{-1} and were iR compensated. The potentials were referenced to SCE which was calibrated with added ferrocene (5×10^{-3} M). The oxidation potential ($E_{1/2}$) values were the average of the anodic and cathodic peak potentials and are listed in Table 2.

Preparative-Scale Electrolysis of Benzyl Alkyl Ethers. The electroxidations were carried out with a PAR Model 173 potentiostat/galvanostat equipped with Model 179 digital coulometer which provided a feedback compensation for ohmic drop between working and the reference electrodes. The voltage-follower amplifier (PAR Model 178) was mounted external 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 ~1.1 cm^3. The anodic coupling of the benzyl ethers was carried out at constant potential.

Catalysis of the Dealkylative Coupling of Benzyl Alkyl Ethers with *Orange* CRET$^{\bullet+}$. General Procedure. A small amount of *Orange* CRET$^{\bullet+}$ (60 mg, 0.10 mmol) was added to a cold (~0 °C) solution of benzyl alkyl ether **1** (1.96 g, 10 mmol) in rigorously dried dichloromethane (50 mL) under an argon atmosphere. The solution immediately turned bright yellow, and it was stirred for half an hour at 0 °C. While warming to room temperature, 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 from hexane afforded the diarylmethane **8** as a crystalline solid in excellent yield (1.52 g, 4.8 mmol, 96%).

The various diarylmethanes listed below were prepared using the general procedure described above and the characteristic spectral data are given.

Bis(4-methyl-2,5-dimethoxyphenyl)methane (8): mp 147–148 °C (lit.[45] mp 147–147.5 °C); ^{1}H NMR (CDCl$_3$) δ 2.22 (s, 6H), 3.71 (s, 6H), 3.80 (s, 6H), 3.92 (s, 2H), 6.64 (s, 2H), 6.71 (s, 2H); ^{13}C NMR (CDCl$_3$) 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 $C_{19}H_{24}O_4$.

Bis(2-methyl-4,5-dimethoxyphenyl)methane (9): mp 121–122 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 2.19 (s, 6H), 3.69 (s, 6H), 3.76 (s, 2H), 3.85 (s, 6H), 6.42 (s, 2H), 6.70 (s, 2H); ^{13}C NMR (CDCl$_3$) 18.96, 35.78, 55.83 (double intensity), 112.76, 113.46, 128.32, 130.33, 146.86; GC–MS 316, M$^+$, 316 calcd for $C_{19}H_{24}O_4$.

Bis(7-methyl-5,8-dimethoxy-1,4-methanotetrahydronaphthyl)methane (10): mp 108–109 °C (MeOH); ^{1}H NMR (CDCl$_3$) δ 1.19 (br d, 4H), 1.44 (br d, 2H), 1.65 (br d, 2H), 1.90 (br d, 4H), 2.09 (s, 3H), 2.10 (s, 3H), 3.32 (s, 3H), 3.35 (s, 3H), 3.53 (br s, 4H), 3.70 (s, 6H), 3.93 (s, 2H); ^{13}C NMR (CDCl$_3$) 12.27, 26.01, 26.06, 27.26, 40.53, 40.89, 48.68, 60.26, 60.38, 60.91, 127.70, 131.39, 137.27, 137.85, 147.84, 148.56; GC–MS 448, M$^+$, 448 calcd for $C_{29}H_{36}O_4$.

Bis(4-methoxymethyl-2,5-dimethoxyphenyl)methane (11): mp 78–79 °C (EtOH); ^{1}H NMR (CDCl$_3$) δ 3.41 (s, 6H), 3.68 (s, 6H), 3.80 (s, 6H), 3.93 (s, 2H), 4.46 (s, 4H), 6.64 (s, 2H), 6.90 (s, 2H); ^{13}C NMR (CDCl$_3$) 29.93, 56.03 (double intensity), 58.32, 69.36, 111.61, 113.42, 124.69, 128.97, 150.84, 151.44; GC–MS 376, M$^+$, 376 calcd for $C_{21}H_{28}O_6$.

Bis(3,4,6-trimethyl-2,5-dimethoxyphenyl)methane (12): mp 142–143 °C (hexane); ^{1}H NMR (CDCl$_3$) δ 2.01(s, 6H), 2.18 (s, 12H), 3.48 (s, 6H), 3.56 (s, 6H), 4.11 (s, 2H); ^{13}C NMR (CDCl$_3$) 12.28, 12.66, 12.84, 25.33, 59.97, 60.36, 127.36, 127.99, 128.07, 131.20, 152.93, 153.13; GC–MS 372, M$^+$, 372 calcd for $C_{23}H_{32}O_4$.

Characterization of Dialkoxymethanes. A solution of benzyl ether **1** (60 mg, 0.3 mmol) in 2 mL anhydrous deuterated dichloromethane (CD_2Cl_2) was treated with a catalytic amount of *Orange* CRET$^{\bullet+}$ (~2 mg) under an argon atmosphere at 0 °C. After usual workup, the CD_2Cl_2 solution was spectrally analyzed (NMR) to show the presence of diarylmethane **8** together with dimethoxymethane [^{1}H NMR (CD_2Cl_2) d 3.25 (s, 6H), 4.47 (s, 2H); ^{13}C NMR (CD_2Cl_2) 54.77, 97.36]. Using this general procedure, described above, a prechilled (~0 °C) solution of phenethyl benzyl ether **2** (572 mg, 2 mmol) was treated with *Orange* CRET$^{\bullet+}$ (12 mg, 0.02 mmol) under an argon atmosphere. The resulting dark yellow solution was stirred for 0.5 h at 0 °C. After workup and removal of the solvent *in vacuo*, the residue was dissolved in deuterated chloroform. The NMR spectra established the presence of diarylmethane **8** (~0.98 mmol) and bis(2-phenylethoxy)methane (0.85 mmol) which was spectrally identical to an authentic sample (*vide infra*). The bis(2-phenylethoxy)methane: oil, ^{1}H NMR (CDCl$_3$) δ 3.97 (t, 4H), 3.81 (t, 4H), 4.76 (s, 2H), 7.30–7.43 (m, 10H); ^{13}C NMR (CDCl$_3$) 35.96, 68.15, 94.77, 125.95, 128.06, 128.62, 138.66. An authentic sample of bis(2-phenylethoxy)methane was prepared by refluxing a 2:1 mixture of 2-phenylethanol (6.1 g, 50 mmol) and paraformaldehyde (0.75 g, 25 mmol) together with a catalytic amount of pyridinium tosylate (50 mg) in toluene (50 mL), with continuous removal of water using a Dean–Stark trap. Usual workup afforded the desired acetal in quantitative yield.

Spectral Measurement of the Radical Cation 1$^{\bullet+}$. A 1 cm quartz cuvette equipped with a sidearm and Teflon needle valve (Schlenk adapter) was charged with a solution of *Orange* CRET$^{\bullet+}$ (2 mL, 0.0001 M) in anhydrous dichloromethane. The solution was cooled in an ice–acetone bath (ca. −15 °C), and a prechilled dichloromethane solution of **1** (0.2 mL, 0.01 M) was added under an argon atmosphere with the aid of a hypodermic syringe. The color of the solution immediately turned bright yellow and afforded UV–vis absorption spectrum shown in Figure 1. The reaction mixture was stirred for 1 h, and the usual workup yielded diarylmethane **8**.

Dealkylative Coupling of Bis(methoxymethyl) Ether 5. A solution of bismethoxymethyl ether **5** (2.26 g, 10 mmol) in anhydrous dichloromethane (50 mL) was cooled in an ice–salt bath and *Orange* CRET$^{\bullet+}$ (60 mg, 0.1 mmol) was added under an argon atmosphere. The solution immediately turned bright yellow, and it was stirred at 0 °C for 0.5 h. The slightly turbid reaction mixture was treated with zinc dust and the mixture was stirred for 5 min. The mixture was filtered and the removal of solvent *in vacuo* left a solid residue which upon chromatographic purification with hexane afforded the desired diarylmethane **11** (0.83 g, 2.21 mmol, 44%) together with unreacted benzyl ether **5** (0.30 g, 1.33 mmol) and traces of a trimeric material (GC–MS 526, M$^+$, 526 calcd for $C_{30}H_{38}O_8$). When an identical reaction mixture of **5** (2.26 g, 10 mmol) in anhydrous dichloromethane (50 mL) and *Orange* CRET$^{\bullet+}$ (50

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[45] Hunt, S. E.; Lindsey, A. S. *J. Chem. Soc.* **1962**, 4550.

mg, 0.1 mmol) was stirred for a longer period of time (6 h), a voluminous precipitate was formed. The colorless precipitate was filtered on a sintered glass funnel and washed repeatedly with dichloromethane. This solid product (1.7 g) was completely insoluble in dichloromethane and chloroform (*vide infra*). The residual filtrate (dichloromethane layer) was evaporated to show the presence of reduced CRET (9,10-dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene), traces of diarylmethane **11**, and the trimeric compound (M^+, 526) as described above.

The Cocoupling of the Bis(methoxymethyl) Ether 5 and the Mono(methoxymethyl) Ether 1. A catalytic amount of *Orange* $CRET^{\bullet+}$ (15 mg, 0.025 mmol) was added to a well-stirred cold (~0 °C) solution of ethers **1** (392 mg, 2 mmol) and **5** (226 mg, 1 mmol) in anhydrous dichloromethane, under an argon atmosphere. The yellow solution was stirred at 0 °C for 6 h. The precipitate formed was removed by filtration under an argon atmosphere and the filtrate was treated with zinc dust as described above. Filtration and removal of solvent *in vacuo* left a crude residue which was fractionally crystallized from a toluene–ether mixture to afford the desired capped trimer **13** (140 mg, 0.30 mmol, 30%) together with the diarylmethane **8** (200 mg, 0.63 mmol, 63%): mp 196–197 °C (lit.[32] mp 196.5–197 °C); ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 6H), 3.69 (s, 6H), 3.70 (s, 6H), 3.78 (s, 6H), 3.90 (s, 4H), 6.63 (s, 2H), 6.65 (s, 2H), 6.69 (s, 2H); ^{13}C NMR ($CDCl_3$) 16.15, 29.68, 55.90, 56.30, 56.35, 113.36, 113.78, 113.86, 124.64, 127.16, 127.51, 151.20, 151.32, 151.45; GC–MS 466, M^+, 466 calcd for $C_{28}H_{34}O_6$.

Degradation of the Polymeric Precipitate with Iodine Monochloride (ICl). The polymeric powder produced in the dealkylative coupling of bis(methoxymethyl) ether **5** (see eqs 4 and 5) was insoluble in most organic solvents (e.g., dichloromethane, chloroform, ethanol, DMSO, DMF, etc.). The polymeric structure for this material with repeating diarylmethane linkage (see eq 4) was deduced from its degradation with iodine monochloride (ICl). Thus, the treatment of diarylmethane **8** (316 mg, 1 mmol) with ICl (405 mg, 2.5 mmol) in dichloromethane (10 mL), according to the procedure of Hubig *et al.*[9] led to a 1:1 mixture of 2-chloro-5-methyl-1,4-dimethoxy-benzene[9] and 2-(chloromethyl)-5-methyl-1,4-dimethoxy-benzene[45] in 89% isolated yield. On the basis of such a facile cleavage of diarylmethane linkage with ICl, we conjectured that the polymeric material (containing diarylmethane linkage as repeating unit) should also lead to a mixture chloroarenes and benzyl chlorides. Indeed, the treatment of the polymeric material with excess ICl in dichloromethane led to a mixture of chloroarenes and benzyl chlorides as follows. [A precise assessment of the number of repeating units (n) in the polymer was not possible by this method.]

General Procedure. The powdered polymeric material (0.75 g), obtained from the dealkylative coupling of benzyl ether **5**, was suspended in anhydrous dichloromethane (25 mL) and iodine monochloride (2.0 g, ~12 mmol) was added with the aid of a hypodermic syringe under an argon atmosphere at room temperature. The dark colored suspension was stirred overnight to afford a homogeneous solution. After evaporation of the solvent, the residue was extracted with ether and washed with aqueous sodium thiosulfate solution followed by saturated brine and dried over anhydrous magnesium sulfate. Removal of the solvent led to an oily residue (0.9 g) which upon GC and GC–MS analysis was found to consist mainly of 2-chloro-5-(chloromethyl)-1,4-dimethoxybenzene (69%), 2,5-dichloro-1,4-dimethoxybenzene (19%), and 2,5-dichloromethyl-1,4-dimethoxybenzene[44] (13%).

Synthesis of Bis[2-(methoxymethyl)-4-methoxy-5-methylphenyl] Crown Ether 17. Preparation of 14. By the literature procedure,[13] $POCl_3$ (10.2 mL) was added dropwise to a stirred mixture of 2-methylanisole (10.5 g, 86 mmol) and DMF (6.0 g). The reaction mixture was heated overnight on a steam bath under reflux to afford a deep brown solution which was cooled and mixed with water (200 mL). Addition of excess of 10% aqueous sodium hydroxide solution led to the separation of a yellow oil which was extracted with ether (3 × 50 mL). The combined ether extracts were washed with water followed by saturated brine, dried over anhydrous magnesium sulfate, and evaporated. The distillation of the crude oil *in vacuo* afforded the pure aldehyde **14** in good yield (10.3 g, 80%).

Preparation of 15.[14] A mixture of the aldehyde **14** (6.4 g, 42 mmol) and *m*-chloroperbenzoic acid (10.9 g, 60 mmol) in anhydrous dichloromethane (200 mL) was heated under reflux for 12 h. The dichloromethane was evaporated *in vacuo*, and the residue was dissolved in ethyl acetate (200 mL). The solution was washed repeatedly with aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. Evaporation of the solvent left the crude formate as an oil, which was dissolved in minimum amount of methanol (25 mL) and a 10% aqueous potassium hydroxide solution (20 mL) was added under an argon atmosphere. The usual workup afforded the pure phenol **15** in excellent yield (5.5 g, 94%).

Preparation of 16. To a solution of 3-methyl-4-methoxyphenol **15** (5.5 g, 40 mmol) in dry tetrahydrofuran (50 mL) was added sodium hydride (1.44 g , 60 mmol), under an argon atmosphere. The reaction mixture was stirred for about 10 min to produce a light brown solution. A solution of tetraethylene glycol di-*p*-tosylate (10.1 g, 20 mmol) in dry tetrahydrofuran (20 mL) was added slowly to the brown mixture under an argon atmosphere. A white solid began to precipitate after 15 min, and heating of the reaction mixture under reflux was continued overnight. The solvent was removed *in vacuo* and the residue was partitioned between dichloromethane and water. The dichloromethane layer was separated and washed repeatedly with dilute hydrochloric acid solution (2%) followed by deionized water. Removal of the solvent *in vacuo* afforded a pale yellow oil which was recrystallized from anhydrous ether to yield the acyclic crown ether **16** (8.2 g, 94%): mp 48–49 °C (ether); ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 6H), 3.70 (sym m, 8H), 3.75 (s, 6H), 3.80 (t, J = 5.1 Hz, 4H), 4.04 (t, J = 5.1 Hz, 4H), 6.64–6.76 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 16.28, 55.69, 67.86, 69.76, 70.56, 70.66, 110.61, 111.58, 117.83, 127.56, 152.02, 152.35; GC–MS 434, M^+, 434 calcd for $C_{24}H_{34}O_7$.

Preparation of 17. A 33% solution of HBr in acetic acid (10 mL) was added dropwise to a well-stirred suspension of paraformaldehyde (1.0 g, 33 mmol) and the crown ether **16** (4.34 g, 10 mmol) in carbon tetrachloride (20 mL).[15] The reaction mixture first turned clear then a light brown color developed. After 2h of stirring, a saturated solution of sodium bicarbonate (25 mL) and dichloromethane (100 mL) was added. The organic layer was separated and washed with aqueous sodium bicarbonate. The dichloromethane layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo* to afford the bis(bromomethyl) crown ether as a clear viscous liquid which was used in the next step without further purification. The bis(bromomethyl) crown ether (6.1 g) was treated with excess sodium methoxide (2.7 g, 50 mmol) in anhydrous methanol (100 mL) at room temperature for 4 h (as described in the general procedure) to afford a viscous oil which was repeatedly washed with dilute hydrochloric acid solution (2%). It was further purified by column chromatography using ether as an eluant to furnish the desired crown ether **17** in excellent yield (4.44 g, 85%): oil, ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 6H), 3.38 (s, 6H), 3.68 (sym m, 8H), 3.76 (s, 6H), 3.79 (t, J = 5.1 Hz, 4H), 4.05 (t, J = 5.1 Hz, 4H), 4.46 (s, 4H), 6.68 (s, 2H), 6.83 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 16.12, 55.70, 58.11, 68.85, 69.03, 69.79, 70.59, 70.64, 110.83, 115.62, 124.94, 126.22, 149.71, 151.90; GC–MS 523, M^+, 523 calcd for $C_{28}H_{42}O_9$.

Cyclization of the Crown Ether 17. As described in the general procedure, a small amount of *Orange* $CRET^{\bullet+}$ (12 mg, 0.02) was added to a cold (~0 °C) solution of crown ether **17** (1.05 g, 2 mmol) in anhydrous dichloromethane (20 mL) under an argon atmosphere. The solution immediately turned bright yellow. A gelatinous material separated form the reaction mixture upon stirring for 1 h at 0 °C. [The gelatinous material was tentatively assigned a linear structure, in which multiple dealkylative coupling occurred *inter*molecularly at each end of **17**.] The dichloromethane layer was carefully decanted under an argon atmosphere and was treated with zinc dust. The mixture was stirred for 5 min and filtered. Removal of the solvent afforded the cyclized *diarylmethane crown* **18** in poor yield (40 mg, ~5%).

In a separate experiment, a mixture of crown ether **17** (1.05 g, 2 mmol) and 1 equiv of sodium hexafluoroantimonate salt in anhydrous dichloromethane (20 mL) was stirred for 1 h at room temperature, under an argon atmosphere. The mixture was cooled in an ice bath (~0 °C) and *Orange* CRET$^{\bullet+}$ (12 mg, 0.02 mmol) was added under an argon atmosphere. The bright yellow color formed immediately, and the mixture was stirred for 1 h. At the end of this period, no gelatinous material was detected. Zinc dust was added and the reaction mixture stirred for 5 min. Zinc dust was filtered off and the colorless solution was evaporated *in vacuo* to afford a viscous residue. The residue was dissolved in ethyl acetate and filtered through a short pad of silica gel. Removal of the solvent *in vacuo* afforded the desired cyclized crown ether **18** as a viscous oil in excellent yield (840 mg, 94%): ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 6H), 3.62 (s, 2H), 3.60–3.70 (m, 8H), 3.68 (s, 6H), 3.74 (m, 4H), 4.06 (m, 4H), 6.45 (s, 2H), 6.69 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 15.88, 28.85, 55.69, 68.83, 69.46, 70.33, 70.87, 112.50, 115.28, 124.21, 127.64, 150.20, 151.58; GC–MS 446, M$^+$, 446 calcd for $C_{25}H_{34}O_7$.

Dealkylative Coupling of Benzyl Alkyl Ethers with Catalytic Amounts of NO$^+$ BF$_4^-$. General Procedure. A Schlenk flask was charged with nitrosonium tetrafluoroborate (23.4 mg, 0.2 mmol) in the dry box and dichloromethane (50 mL) added with the aid of a hypodermic syringe. [Note that the NO$^+$ salt is insoluble in dichloromethane.] The slurry was cooled in an ice bath (~0 °C) and benzyl methyl ether **6** (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 **12** as the sole product (3.5 g, 94%). The other benzyl ethers in Table 1 were similarly treated in dichloromethane with catalytic amounts of $NO^+BF_4^-$ (or the $SbCl_6^-$ salt) to afford the corresponding diarylmethanes in excellent yields.

Electrocatalysis of the Dealkylative Coupling of Benzyl Alkyl Ethers. General Procedure. 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 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 **8** (300 mg, 0.95 mmol) in excellent yield (23, 160% based on the amount of current passed through the solution.

Inhibition of the Dealkylative Coupling of Benzyl Alkyl Ethers. Zinc Dust. A prechilled (~0 °C) dichloromethane solution of *Orange* CRET$^{\bullet+}$ (2 mL, 0.01 M) in an ice–salt bath was added to a cold (~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. The both reaction mixtures were stirred for 0.5 h. The control (without zinc dust) was quenched with zinc dust. After stirring for an additional 2 min both reaction mixtures were individually filtered and the solvent removed *in vacuo*. The residues were analyzed by GC using internal standard method. Thus, the portion without added zinc showed complete conversion of **1** to the diarylmethane **8** (152 mg, 96%), whereas the portion containing zinc dust showed a partial conversion to diarylmethane **8** (28 mg, 18%) and 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* CRET$^{\bullet+}$ (0.01 M, 2 mL) in dichloromethane was prepared at 0 °C as described above. After stirring for 2 min, a prechilled (~0 °C) solution of octamethylbiphenylene[16] (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 ocatmethylbiphenylene radical cation with characteristic absorbances at λ_{max} = 600 and 550 (sh) nm.[17] The reaction mixture was stirred for an additional 0.5 h, and zinc dust was added. After stirring for an additional 2 min, the mixture was filtered and solvent removed *in vacuo* to afford a residue which upon GC analysis showed only partial conversion to diarylmethane **8** (80 mg, 25%). The remainder of the starting material and octamethylbiphenylene were recovered unchanged.

Tetra-*n*-butylammonium Iodide. A similar reaction mixture of **1** (20 mL, 2 mmol, 0.1 M) and *Orange* CRET$^{\bullet+}$ (2 mL, 0.01 M) in dichloromethane was stirred at 0 °C for 2 min, and a cold solution of tetra-*n*-butylammonium iodide (37 mg, 0.1 mmol) in dichloromethane (2 mL) was added. The solution immediately turned pale brown and was further stirred for 0.5 h. Evaporation of the solvent *in vacuo* afforded a residue which was dissolved in hexane and filtered through a short pad of silica gel. GC analysis of the filtrate showed only a partial conversion to diarylmethane **8** (89 mg, 28%) and remainder of the starting material was recovered unchanged.

Effect of the Solvent and Acids on the Dealkylative Coupling of Benzyl Methyl Ether 1. Acetonitrile. A solution of benzyl methyl ether **1** (392 mg, 2 mmol) in dry acetonitrile (10 mL) was cooled in an ice–salt bath, and *Orange* CRET$^{\bullet+}$ (12 mg, 0.02 mmol) was added under an argon atmosphere. The solution immediately turned bright yellow, and it was stirred at 0 °C for 0.75 h as the colorless crystals of diarylmethane **8** separated. The reaction mixture was treated with aqueous sodium bicarbonate and was extracted with diethyl ether. The ether layer was dried over anhydrous magnesium sulfate and removal of solvent *in vacuo* yielded a solid residue which upon recrystallization from ethanol afforded the pure diarylmethane **8** (310 mg, 98%). A similar yellow colored reaction mixture of ether **1** (392 mg, 2 mmol) and *Orange* CRET$^{\bullet+}$ (12 mg, 0.02 mmol) in acetonitrile was stirred at 0 °C for 0.75 h and was treated with a pinch of zinc dust. The mixture was stirred for 5 min and the colorless solution was diluted with ether (50 mL) and filtered. The ether layer was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded the pure diarylmethane **8** (306 mg, 97%).

Wet Acetonitrile. A solution of benzyl methyl ether **1** (392 mg, 2 mmol) in acetonitrile (10 mL) containing water (0.1 mL) was treated with *Orange* CRET$^{\bullet+}$ (48 mg, 0.08 mmol) at 0 °C. The solution immediately developed a characteristic bright yellow coloration. The yellow color slowly faded and a colorless solution was obtained (~5 min). The reaction mixture was stirred for an additional 5 min and was quenched with aqueous sodium bicarbonate. The standard workup yielded an oily residue, which upon GC and GC–MS (internal standard) analysis was shown to be consisted of diarylmethane **8** (212 mg, 0.67 mmol, 67%) and benzyl methyl ether **1** (119 mg, 0.6 mmol, 30%). In a control experiment, a similar mixture of benzyl ether **1** (392 mg, 2 mmol) and *Orange* CRET$^{\bullet+}$ (48 mg, 0.08 mmol) in 10 mL of dry acetonitrile (without added water) was stirred for 10 min. The standard aqueous quench/workup as described above, afforded the crystalline diarylmethane **8** in essentially quantitative yield (309 mg, 98%). [Note that a solution of the parent 2,5-dimethyl-1,4-dimethoxybenzene radical cation, prepared from *Orange* CRET$^{\bullet+}$ (48 mg, 0.08 mmol) and the neutral donor (166 mg, 1 mmol) in acetonitrile containing 1% v water, slowly faded to a colorless solution over a 8 min period.]

Methanol. To a cold (0 °C) solution of benzyl methyl ether **1** (392 mg, 2 mmol) in anhydrous methanol (10 mL), under an argon atmosphere, was added *Orange* CRET$^{\bullet+}$ (12 mg, 0.02 mmol). The reaction mixture developed a transient yellow coloration which bleached within seconds. The colorless mixture was stirred for 30 min and then treated with aqueous sodium bicarbonate. The usual workup afforded the crude oily residue. The GC and GC–MS analysis showed that the residue consisted of mainly benzyl methyl ether **1** (372, 1.90 mmol, 95%) and traces of unidentified products. In a similar experiment, a solution of parent 2,5-dimethyl-1,4-dimethoxybenzene (166 mg, 1 mmol) in methanol (10 mL)was treated with *Orange* CRET$^{\bullet+}$ (12 mg, 0.02 mmol) at 0 °C. The transient yellow color similarly bleached within seconds. [Note that the 2,5-dimethyl-1,4-dimethoxybenzene radical cation was persistent for days in anhydrous dichloromethane.]

Effect of Pyridine. A solution of benzyl methyl ether **1** (392 mg, 2 mmol) and pyridine (158 mg, 2 mmol) in dry acetonitrile (10 mL) was treated with *Orange* CRET$^{\bullet+}$ (12 mg, 0.02 mmol) at −10 °C, under an argon atmosphere. The reaction mixture immediately took on a transient yellow coloration which faded rapidly. The mixture was stirred for 30 min and the aqueous quench/workup as above, afforded an oily residue which upon GC and GC–MS analysis (internal standard method) showed that the benzyl methyl ether **1** (385 mg, 98%) was recovered intact. In a control experiment, a solution of 2,5-dimethyl-1,4-dimethoxybenzene (166 mg, 1 mmol) and pyridine (79 mg, 1 mmol) in anhydrous acetonitrile (5 mL) was treated with *Orange* CRET$^{\bullet+}$ (12 mg, 0.02 mmol) at −10 °C. The yellow coloration faded rapidly. [Note that the 2,5-dimethyl-1,4-dimethoxybenzene radical cation was stable for prolonged periods in anhydrous acetonitrile in absence of pyridine.]

Tetrafluoroboric Acid (HBF_4). An acetonitrile solution (0.2 mL, 0.1 M) of freshly prepared HBF_4 (from silver tetrafluoroborate and anhydrous hydrogen chloride) was added to a cold (~0 °C) solution of benzyl methyl ether **1** (392 mg, 2 mmol) in dry acetonitrile (10 mL) under an argon atmosphere. The pale yellow solution was stirred at 0 °C for 45 min. The reaction mixture was quenched with aqueous sodium bicarbonate and extracted with diethyl ether (3 × 25 mL). The ether layer was dried over anhydrous magnesium sulfate. The removal of the solvent *in vacuo* left a crude residue, which upon GC and GC–MS analysis (internal standard method) indicated a mixture of diarylmethane **8** (227 mg, 0.72 mmol, 72%) and benzyl methyl ether **1** (96 mg, 0.49 mmol, 25%).

Trifluoromethanesulfonic Acid (CF_3SO_3H). In a similar experiment, a solution of trifluoromethanesulfonic acid in acetonitrile (0.2 mL, 0.1 M) was added to a solution of ether **1** (392 mg, 2 mmol) in dry acetonitrile (10 mL) at 0 °C. The pale yellow reaction mixture was stirred for 45 min and then quenched as described above. The GC and GC–MS analysis of the ethereal extracts indicated a mixture of diarylmethane **8** (246 mg, 0.78 mmol, 78%) and benzyl methyl ether **1** (79 mg, 0.4 mmol, 20%).

Hydrogen Bromide (HBr). A cold (0 °C) solution of benzyl methyl ether **1** (392 mg, 2 mmol) in acetonitrile (10 mL) was treated with a solution of anhydrous hydrogen bromide in acetonitrile (0.4 mL, 0.12 M), under an argon atmosphere. The colorless reaction mixture was stirred at 0 °C for 1 h. The standard aqueous quench/workup, as described above, afforded an oily residue, which upon GC and GC–MS analysis showed the residue to consist of benzyl methyl ether **1** (368 mg, 1.88 mmol, 94%) and traces of 2-(bromomethyl)-5-methyl-1,4-dimethoxybenzene (29 mg, 0.12 mmol).[43] In a similar experiment, a mixture of benzyl methyl ether **1** (392 mg, 2 mmol) in acetonitrile (10 mL) and saturated acetonitrile solution of anhydrous HBr (2 mL) was stirred at 0 °C for 30 min. The aqueous workup afforded 2-(bromomethyl)-5-methyl-1,4-dimethoxybenzene,[43] identified by (GC and GC–MS) comparison with an authentic sample (*vide supra*), in essentially quantitative yield (485 mg).

Wet Acetonitrile and Acid. A solution of benzyl methyl ether **1** (392 mg, 2 mmol) in acetonitrile (10 mL) containing water (0.1 mL) was treated with tetrafluoroboric acid (0.4 mL, 0.1M) at 0 °C. The colorless reaction mixture was stirred for 10 min, and it was quenched with aqueous sodium bicarbonate. The standard workup yielded an oily residue, which upon GC and GC–MS analysis indicated a mixture of diarylmethane **8** (63 mg, 0.2 mmol, 20%) and benzyl methyl ether **1** (302 mg, 1.54 mmol, 77%). In a control experiment, a similar mixture of benzyl ether **1** (392 mg, 2 mmol) and tetrafluoroboric acid (0.4 mL, 0.1M) in 10 mL dry acetonitrile (without added water) was stirred for 10 min. The standard aqueous quench/workup, as described above, afforded the crystalline diarylmethane **8** in essentially quantitative yield (306 mg, 97%). In another similar experiment, a solution of benzyl methyl ether **1** (392 mg, 2 mmol) in acetonitrile (10 mL) containing larger amounts of water (0.5 mL) was treated with tetrafluoroboric acid (0.4 mL, 0.1 M). The colorless solution was stirred for 10 min and quenched as described above to afford an oily residue. GC and GC–MS analysis showed that benzyl methyl ether **1** was recovered intact (382 mg, 1.95 mmol, 97%).

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Supporting Information Available: The ^{13}C NMR spectra for compounds **1–3**, **7–12**, and **16–18** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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