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Electron-Transfer-Induced Intermolecular [2 + 2] Cycloaddition Reactions Based on the Aromatic "Redox Tag" Strategy

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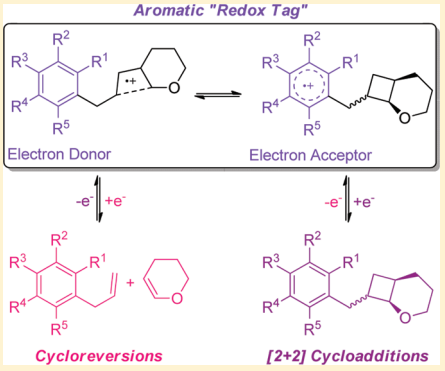
Supporting Information

ABSTRACT: Novel electron-transfer-induced intermolecular [2 + 2] cycloaddition reactions between an aliphatic cyclic enol ether and several unactivated olefins have been demonstrated on the basis of the aromatic "redox tag" strategy. The aromatic "redox tag" was oxidized during the formation of the cyclobutane ring, affording the relatively long-lived aromatic radical cation, which was then reduced to complete the overall reaction that constructed the corresponding [2 + 2] cycloadducts. The aromatic "redox tag" was also found to facilitate electron-transfer-induced cycloreversion reactions of cyclobutane rings.

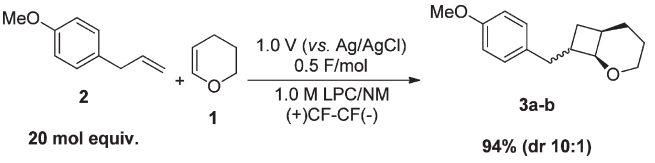


INTRODUCTION

Cycloaddition reactions are intriguing both synthetically and mechanistically. To date, numerous elegant synthetic strategies based on the cycloaddition reactions have been established to construct a wide variety of ring systems.[1] One can also access the vast number of clear-cut mechanistic studies on the cycloaddition reactions.[2] Furthermore, cycloreversion reactions have also been widely investigated because of their practical and theoretical potentials.[3] In particular, electron-transfer-induced [2 + 2] cycloaddition reactions have extensively been studied.[4] In order to generate radical ion intermediates, photochemical processes are widely employed.[5] One-electron oxidants and reductants can also be used to produce radical ions.[6] In this context, electrochemical processes have been utilized to trigger either one or two electron transfers that afford radical ion intermediates in unique ways.[7] The notable insights have also been made into [2 + 2] cycloaddition reactions, providing a powerful tool for the rational design of novel cycloaddition reactions.[8] In this respects, electron transfer-induced cycloreversion reactions of four-membered ring have been represented through radical ion intermediates,[9] which appear to be involved in DNA lesions, allowing biological processes to be probed.[10]

We have previously developed electron-transfer-induced intermolecular [2 + 2] cycloaddition reactions between enol ethers and unactivated olefins.[11] For example, the anodically generated radical cation of 3,4-dihydro-2*H*-pyran (**1**) was trapped by 4-allylanisole (**2**) to give the corresponding [2 + 2] cycloadducts **3a**,**b** in excellent yield as diastereomeric mixtures (Scheme 1). Because of the short lifetime of the enol ether radical cation,[12] an excess of **2** was essential to trap the radical cation of **1** to afford **3a**,**b**, which should also be a driving force of the reaction. The oxidation potential of **1** (E_p^{ox} = 1.41 V vs Ag/AgCl) was lower than that of **2** (E_p^{ox} = 1.51 V vs Ag/AgCl), enabling the selective anodic oxidation of **1**. Since no [2 + 2] cycloadduct was obtained when allylbenzene was used in place of **2**, even in the presence of a large excess of anisole (**4**), the alkoxyphenyl group was proven to be essential for the reaction, serving as a "redox tag" (Scheme 2). Thus, the alkoxyphenyl group was oxidized during the formation of the cyclobutane ring, affording the relatively long-lived alkoxyphenyl radical cation, which was then reduced to complete the overall reaction (Scheme 3).[13] With these results in hand, we sought to find new electron-transfer-induced intermolecular [2 + 2] cycloaddition reactions based on the aromatic "redox tag" strategy (Scheme 4).

Scheme 1. Electron-Transfer-Induced Intermolecular [2 + 2] Cycloaddition Reaction between 3,4-Dihydro-2*H*-pyran (1) and 4-Allylanisole (2)



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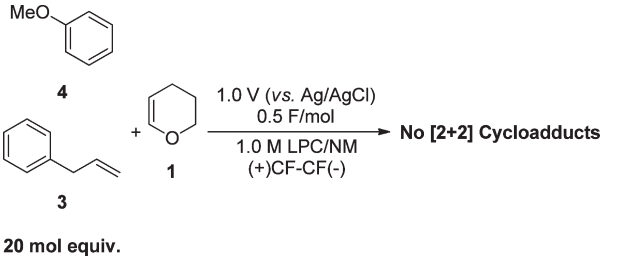
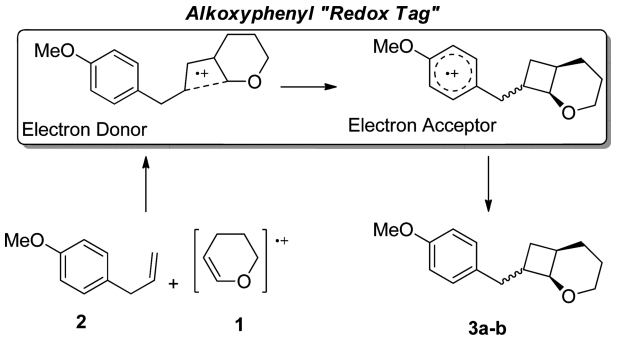
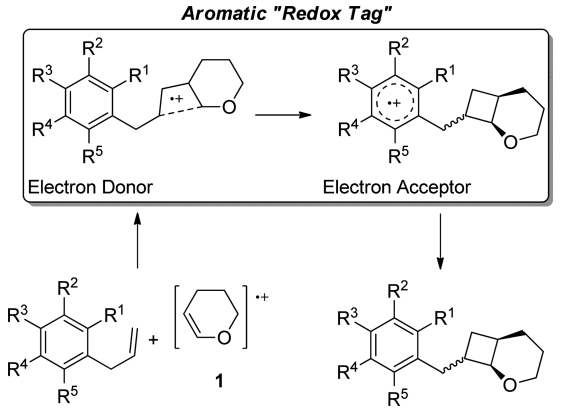
Scheme 2. Anodic Oxidation of 3,4-Dihydro-2*H*-pyran (1) in the Presence of an Excess of Allylbenzene (3) and Anisole (4)



Scheme 3. Plausible Function of Alkoxyphenyl "Redox Tag"



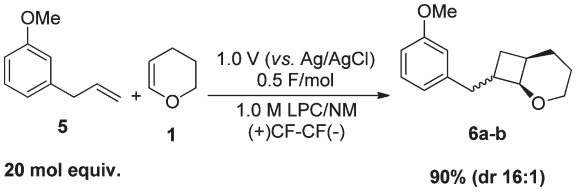
Scheme 4. New Electron-Transfer-Induced Intermolecular [2 + 2] Cycloaddition Reactions Based on Aromatic "Redox Tag" Strategy



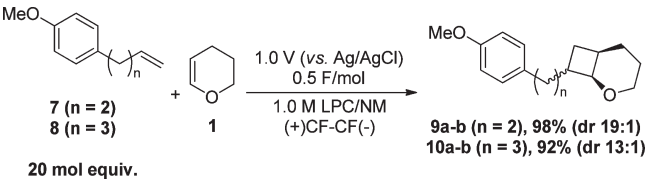
RESULTS AND DISCUSSION

The present work began with the preparation of 3-allylanisole (**5**).[14] The anodic oxidation of **1** was attempted in the presence of an excess of **5** to give the corresponding [2 + 2] cycloadducts **6a**, **b** in excellent yield as diastereomeric mixtures (Scheme 5). This observation indicated that there were little positional effects of the substituent on the aromatic "redox tag." In addition, both 4-(but-3-enyl)anisole (**7**) and 4-(pent-4-enyl)anisole (**8**) also efficiently trapped the radical cation of **1** to give the corresponding [2 + 2] cycloadducts **9a**,**b** and **10a**,**b**, respectively, in excellent yields as diastereomeric mixtures, indicating that the

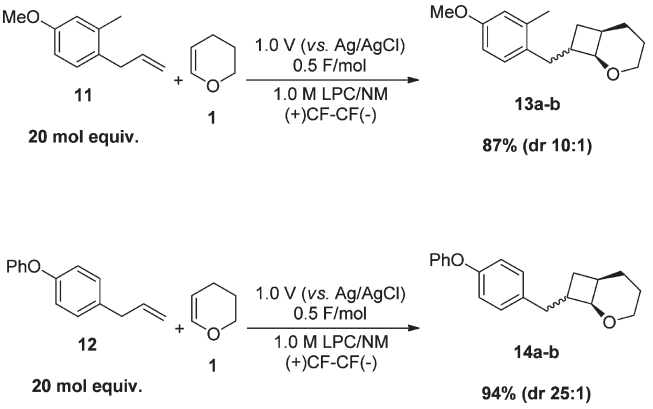
Scheme 5. Electron-Transfer-Induced Intermolecular [2 + 2] Cycloaddition Reaction between 3,4-Dihydro-2*H*-pyran (1) and 3-Allylanisole (5)



Scheme 6. Electron-Transfer-Induced Intermolecular [2 + 2] Cycloaddition Reactions between 3,4-Dihydro-2*H*-pyran (1) and Alkenylanisoles 7 and 8



Scheme 7. Electron-Transfer-Induced Intermolecular [2 + 2] Cycloaddition Reactions between 3,4-Dihydro-2*H*-pyran (1) and Alkoxyallylbenzenes 11 and 12



alkoxyphenyl group functioned as a "redox tag" even though it was positioned remotely from the cyclobutyl moiety (Scheme 6). Moreover, both 4-allyl-2-methylanisole (**11**) and 1-allyl-4-phenoxybenzene (**12**) effectively trapped the radical cation of **1** to afford the corresponding [2 + 2] cycloadducts **13a**,**b** and **14a**,**b**, respectively, in excellent yields as diastereomeric mixtures (Scheme 7). However, no corresponding [2 + 2] cycloadducts were obtained when 4-allyl-*N*,*N*-dimethylaniline (**15**) or 4-allylthioanisole (**16**) were used in place of **2**, suggesting that neither aminophenyl group nor thiophenyl group could function as aromatic "redox tag" (Scheme 8). On the other hand, alkylphenyl group was found to facilitate the electron transfers through the reactions, constructing the corresponding [2 + 2] cycloadducts. The efficiencies of the alkylphenyl "redox tags" significantly relied on the number of the alkyl substituent (Scheme 9). These results could be rationalized based on the oxidation potentials of the substrates (Table 1). Thus, there was

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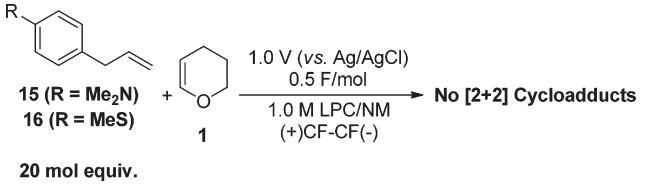
Scheme 8. Anodic Oxidation of 3,4-Dihydro-2*H*-pyran (1) in the Presence of an Excess of 4-Allyl-*N*,*N*-dimethylaniline (15) or 4-Allylthioanisole (16)



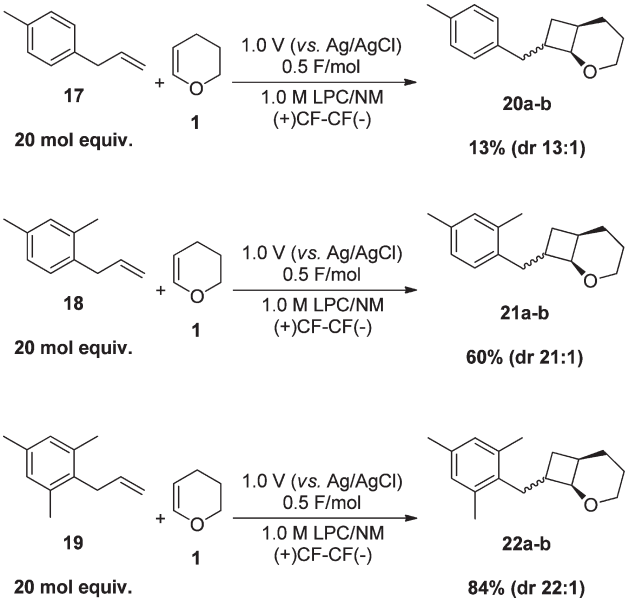
an appropriate value of the oxidation potentials for the aromatic ring to function as a "redox tag"; namely, the lower oxidation potentials were favorable, as long as higher than that of **1** (Figure 1). In principle, it was perhaps fair to say that novel electron-transfer-induced intermolecular [2 + 2] cycloaddition reactions could be designed through simply measuring oxidation potentials, enabled by the aromatic "redox tag" strategy.

The electron impact mass spectrum of **3a** (*trans*-isomer) showed a fragmentation pattern that displayed a base peak at *m*/*z* 148, which could be assigned to the radical cation of **2** (Figure S1, Supporting Information). This result suggested that the high energy radical cation of **3a** that was produced in the mass spectrometer participated in the cycloreversion reaction of the cyclobutane ring. The oxidation potential of **3a** (E_p^{ox} = 1.54 V vs Ag/AgCl) was close to that of 4-propylanisole (**26**) (E_p^{ox} = 1.49 V vs Ag/AgCl), indicating that **3a** and **26** could each be oxidized on the alkoxyphenyl group to generate the corresponding radical cations (Scheme S1, Supporting Information).

With these results in hand, the anodic oxidation of **3a** was attempted to give the cycloreversion product **2** in moderate yield (Scheme 10). Although the reaction was highly chemoselective, the isolated yield was moderate because the anodic oxidation of **2** must occur in competition with that of **3a** under reaction condition, leading to its decomposition (Scheme S2, Figures S2 and S3, Supporting Information). Through careful examination of the reaction mixture, we also found that the cycloreversion reaction of **3a** was accompanied by the formation of a small amount of **3b** (*cis*-isomer), strongly verifying that the radical cation generated on the alkoxyphenyl group contributed the cleavage of the carbon−carbon bond that constitutes the cyclobutane ring (Scheme 11). This reaction was suspected to be accompanied by the formation of radical cation of **1**, possibly resulting in decomposition. The cycloreversion reactions of **9a** and **10a** were also anodically induced (Scheme 12). The oxidation potentials of **13a** (E_p^{ox} = 1.50 V vs Ag/AgCl) and **14a** (E_p^{ox} = 1.45 V vs Ag/AgCl) were both similar to that of **26**, indicating that the alkoxyphenyl group was serving as the "redox tag" to facilitate the generation of the corresponding radical cation through anodic oxidation. Moreover, the anodic oxidation of **22a** was attempted to give the cycloreversion product **19** in moderate yield, suggesting that the trimethylphenyl group was also serving as the "redox tag" to trigger the cycloreversion reaction through the production of the corresponding radical cation (Scheme 13).

We subsequently carried out the anodic oxidation of **3a** in the presence of an excess of **7** that led to the formation of **9a**,**b**, accompanied by the formation of **2**. This result suggested that the radical cation of **1** was released from **3a**, which was then trapped by **4** in a crossover reaction (Scheme 14). In this case, the amount of **2** derived from the cycloreversion reaction of **3a** was not expected to be sufficient to retrap the radical cation of **1**.

Scheme 9. Electron-Transfer-Induced Intermolecular [2 + 2] Cycloaddition Reactions between 3,4-Dihydro-2*H*-pyran (1) and Alkylallylbenzenes 17−19



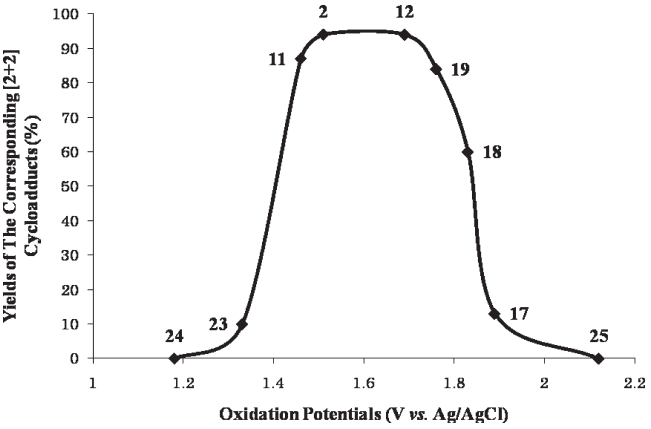
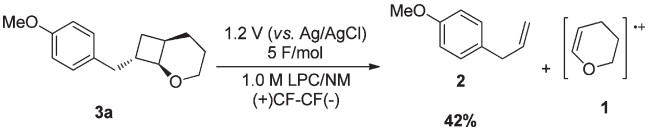


Figure 1. Relationship between the oxidation potentials of the substrates and the yields of the corresponding [2 + 2] cycloadducts.

Scheme 10. Electron-Transfer-Induced Cycloreversion Reaction of the [2 + 2] Cycloadduct 3a



Finally, the spin distribution of the radical cation of **3a** was calculated. It was observed that the spin was not localized entirely on the alkoxyphenyl group, but was also distributed onto the cyclobutyl moiety (Figure 2). This observation was contrasting with the spin distribution of the radical cation of the [2 + 2] cycloadduct **27**.[13] Indeed, the anodic oxidation of **27** gave **2** only in low yield and might be accompanied by the formation of the

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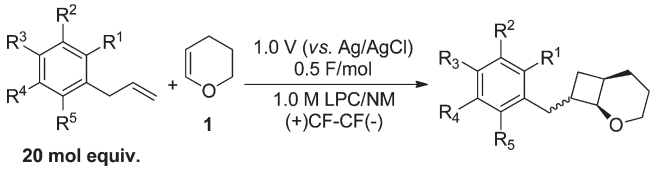
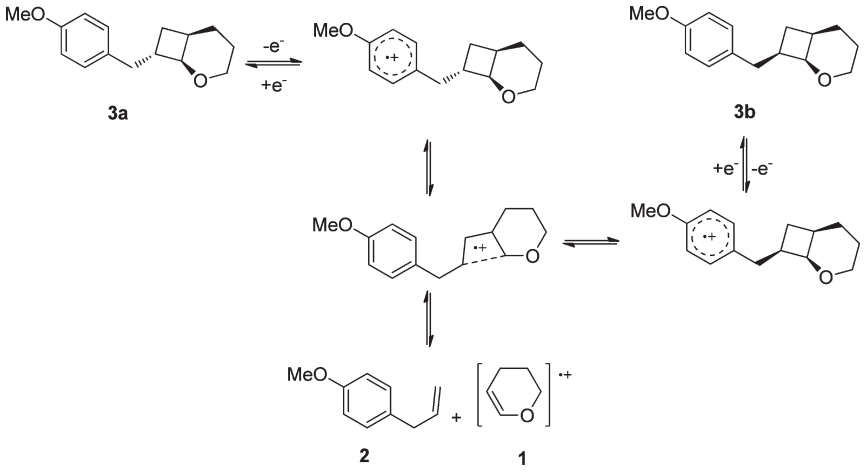
Table 1. Oxidation Potentials of the Substrates Used



substrates	oxidation potentials (vs Ag/AgCl)	yield[a] (%)
24 (R^1 = H, R^2 = MeO, R^3 = MeO, R^4 = MeO, R^5= H)	E_p^{ox} = 1 18 V	trace
23 (R^1 = H, R^2 = MeO, R^3 = MeO, R^4 = H, R^5= H)	E_p^{ox} = 1 33 V	10
1	E_p^{ox} = 1 41 V	
11 (R^1 = Me, R^2 = H, R^3 = MeO, R^4 = H, R^5 = H)	E_p^{ox} = 1 46 V	87
2 (R^1 = H, R^2 = H, R^3 = MeO, R^4 = H, R^5 = H)	E_p^{ox} = 1 51 V	94
12 (R^1 = H, R^2 = H, R^3 = PhO, R^4 = H, R^5 = H)	E_p^{ox} = 1 69 V	94
19 (R^1 = Me, R^2 = H, R^3 = Me, R^4 = H, R^5 = Me)	E_p^{ox} = 1 76 V	84
18 (R^1 = Me, R^2 = H, R^3 = Me, R^4 = H, R^5 = H)	E_p^{ox} = 1 83 V	60
17 (R^1 = Me, R^2 = H, R^3 = H, R^4 = H, R^5 = H)	E_p^{ox} = 1 89 V	13
25 (R^1 = H, R^2 = H, R^3 = H, R^4 = H, R^5 = H)	E_p^{ox} = 2 12 V	n.d.

[a] Yields of the corresponding [2 + 2] cycloadducts determined by NMR.

Scheme 11. Plausible Reaction Mechanism of the Electron-Transfer-Induced Cycloreversion Reaction of the [2 + 2] Cycloadduct 3a



radical cation of **28** (Scheme 15). Apparently, the ring strain of the bicyclic structure was also responsible for driving the cycloreversion reactions.

CONCLUSION

In conclusion, we have demonstrated novel electron-transfer-induced intermolecular [2 + 2] cycloaddition reactions based on the aromatic "redox tag" strategy. The anodically generated radical cation of an aliphatic cyclic enol ether was effectively trapped by several unactivated olefins possessing aromatic "redox tag" to construct the corresponding [2 + 2] cycloadducts. The aromatic "redox tag" was oxidized during the formation of the cyclobutane ring, affording the relatively long-lived aromatic radical cation, which was then reduced to complete the overall reaction. Furthermore, aromatic "redox tag" was also found to facilitate the generation of the corresponding radical cations through anodic oxidation, which then induced electron-transfer-induced cycloreversion reactions of cyclobutane rings.

EXPERIMENTAL SECTION

[2 + 2] Cycloaddition Reactions. Olefins possessing an alkoxyphenyl group (4.0 mmol) and aliphatic enol ethers (0.20 mmol) were added to 1.0 M $LiClO_4/CH_3NO_2$ (20 mL). The undivided reaction cell was capped with a septum equipped with the carbon felt anode (20 mm × 20 mm), carbon felt cathode (20 mm × 20 mm), and the Ag/AgCl reference electrode. The electrolysis was then performed at 1.0 V (vs. Ag/AgCl). After the reaction was completed, the reaction mixture was poured into EtOAc, and the EtOAc solution was successively washed with brine. The organic layer was dried over anhydrous $MgSO_4$. After filtration and evaporation under reduced pressure, the residue was purified by silica gel column chromatography using *n*-hexane−EtOAc to give cycloadducts. The products yields were determined by NMR.

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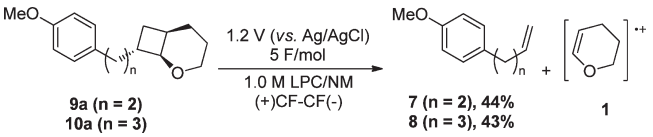
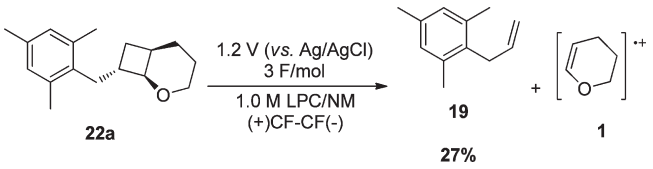
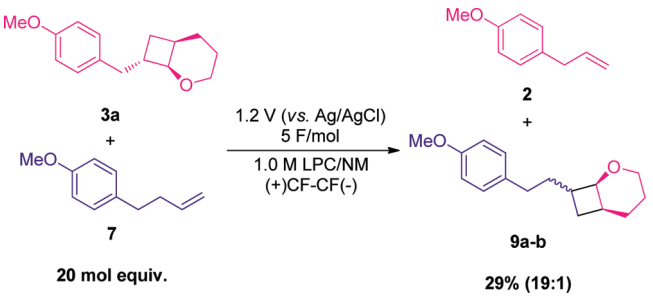
Scheme 12. Electron-Transfer-Induced Cycloreversion Reactions of the [2 + 2] Cycloadducts 9a−10a



Scheme 13. Electron-Transfer-Induced Cycloreversion Reaction of the [2 + 2] Cycloadduct 22a



Scheme 14. Electron-Transfer-Induced Crossover [2 + 2] Cycloaddition Reaction between the [2 + 2] Cycloadduct 3a and 4-(But-3-enyl)anisole (7)



Cycloreversion Reactions. [2 + 2] Cycloadducts (0.10 mmol) were added to 1.0 M $LiClO_4/CH_3NO_2$ (20 mL). The undivided reaction cell was capped with a septum equipped with the carbon felt anode (20 mm × 20 mm), carbon felt cathode (20 mm × 20 mm), and the Ag/AgCl reference electrode. The electrolysis was then performed at 1.2 V (vs. Ag/AgCl). After the reaction was completed, the products yields were determined by GC−MS.

*8-(4-Methoxybenzyl)-2-oxabicyclo[4.2.0]octane (**3a**) (trans, major):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.08 (2H, d, J = 8.8 Hz), 6.82 (2H, d, J = 8.8 Hz), 3.87 (1H, t, J = 6.6 Hz), 3.78 (3H, s), 3.73−3.65 (1H, m), 3.63−3.56 (1H, m), 2.88−2.78 (2H, m), 2.58 (1H, dd, J = 15.4, 10.3 Hz), 2.40−2.30 (1H, m), 1.96−1.86 (1H, m), 1.72−1.64 (1H, m), 1.60−1.51 (1H, m), 1.51−1.42 (2H, m), 1.42−1.34 (1H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.7, 132.9, 129.5, 113.7, 74.7, 63.0, 55.2, 39.4, 38.8, 30.4, 26.8, 25.7, 23.3; IR (NaCl, cm^{-1}) 2933, 2845, 1612, 1513, 1247, 1109, 1037, 837; MS (rel int) m/z 232 (M^+, 12), 148 (83), 133 (53), 121 (100), 105 (35), 84 (65); HRMS calcd for $C_{15}H_{20}O_2$ 232.1463 (M + H 233.1542), found 233.1527

*8-(4-Methoxybenzyl)-2-oxabicyclo[4.2.0]octane (**3b**) (cis, minor):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.11 (2H, d, J = 8.8 Hz), 6.80 (2H, d, J = 8.8 Hz), 4.11 (1H, dd, J = 8.1, 4.4 Hz), 3.92−3.87 (1H, m), 3.78 (3H, s), 3.25−3.18 (1H, m), 2.82 (1H, dd, J = 13.9, 8.1 Hz), 2.54 (1H, dd, J = 13.9, 8.1 Hz), 2.34−2.24 (1H, m), 2.18−2.09 (1H, m), 1.99 (1H, dd, J = 20.5, 10.3 Hz), 1.91−1.84 (1H, m), 1.84−1.77 (1H, m), 1.60−1.49 (2H, m), 1.47−1.40 (1H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.5, 133.8, 129.5, 113.6, 75.0, 64.7, 55.2, 39.3, 33.7, 30.2, 29.1, 23.4, 21.7; IR (NaCl, cm^{-1}) 2933, 2849, 1612, 1512, 1245, 1176, 1040, 833; MS (rel int) m/z 232 (M^+, 12), 148 (90), 133 (47), 121 (100), 105 (32), 84 (68); HRMS calcd for $C_{15}H_{20}O_2$ 232.1463 (M + H 233.1542), found 233.1539.

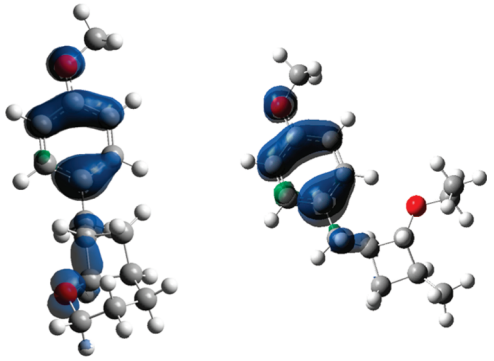
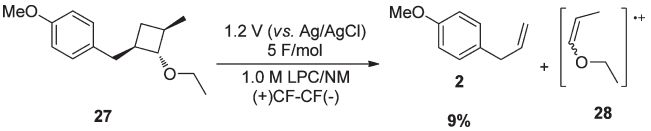


Figure 2. Spin distributions of the radical cation of **3a** (left) and that of **27** (right).

Scheme 15. Electron-Transfer-Induced Cycloreversion Reaction of the [2 + 2] Cycloadduct 27



*8-(3-Methoxybenzyl)-2-oxabicyclo[4.2.0]octane (**6a**) (trans, major):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.19 (1H, t, J = 8.1 Hz), 6.77 (1H, d, J = 8.1 Hz), 6.75−6.69 (2H, m), 3.89 (1H, t, J = 6.6 Hz), 3.79 (3H, s), 3.74−3.66 (1H, m), 3.65−3.56 (1H, m), 2.95−2.82 (2H, m), 2.68−2.55 (1H, m), 2.43−2.30 (1H, m), 1.98−1.84 (1H, m), 1.75−1.63 (1H, m), 1.62−1.44 (3H, m), 1.44−1.35 (1H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 159.5, 142.5, 129.2, 121.0, 114.3, 111.1, 74.7, 63.0, 55.1, 39.8, 39.0, 30.5, 26.9, 25.7, 23.3; IR (NaCl, cm^{-1}) 2937, 2845, 1733, 1600, 1489, 1262, 1105, 779; MS (rel int) m/z 232 (M^+, 1), 148 (100), 133 (14), 117 (33), 105 (11), 84 (32); HRMS calcd for $C_{15}H_{20}O_2$ 232.1463 (M + H 233.1542), found 233.1538.

*8-[2-(4-Methoxyphenyl)ethyl]-2-oxabicyclo[4.2.0]octane (**9a**) (trans, major):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.09 (2H, d, J = 8.8 Hz), 6.82 (2H, d, J = 8.8 Hz), 3.82 (1H, t, J = 7.3 Hz), 3.79 (3H, s), 3.72−3.57 (2H, m), 2.67−2.48 (3H, m), 2.40−2.29 (1H, m), 1.99−1.86 (1H, m), 1.85−1.74 (1H, m), 1.73−1.61 (2H, m), 1.56−1.43 (3H, m), 1.35−1.24 (1H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.6, 134.6, 129.3, 113.7, 75.5, 62.9, 55.3, 37.5, 36.2, 32.8, 30.5, 27.0, 25.9, 23.4 IR (NaCl, cm^{-1}) 2932, 2851, 1611, 1513, 1247, 1111, 1038, 822; MS (rel int) m/z 246 (M^+, 1), 162 (67), 121 (100), 84 (27), 69 (19), 55 (11); HRMS calcd for $C_{16}H_{22}O_2$ 246.1620 (M + H 247.1698), found 247.1703.

*8-[2-(4-Methoxyphenyl)ethyl]-2-oxabicyclo[4.2.0]octane (**9b**) (cis, minor):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.09 (2H, d, J = 8.1 Hz), 6.81 (2H, d, J = 8.1 Hz), 4.16−4.08 (1H, m), 3.89−3.81 (1H, m), 3.78 (3H, s), 3.24−3.15 (1H, m), 2.57−2.42 (2H, m), 2.21−2.11 (1H, m), 1.94−1.85 (2H, m), 1.85−1.72 (2H, m), 1.71−1.61 (1H, m), 1.57−1.47 (2H, m), 1.46−1.37 (1H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.5, 135.0, 129.3, 113.6, 75.1, 64.6, 55.3, 37.0, 32.6, 30.4, 30.2, 29.0, 23.5, 21.8; IR (NaCl, cm^{-1}) 2932, 2852, 1613, 1513, 1246, 1177, 1048, 826; MS (rel int) m/z 162 (28), 134 (1), 121 (100), 84 (15), 69 (8), 55 (7); HRMS calcd for $C_{16}H_{22}O_2$ 246.1620 (M + H 247.1698), found 247.1698.

*8-[3-(4-Methoxyphenyl)propyl]-2-oxabicyclo[4.2.0]octane (**10a**) (trans, major):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.09 (2H, d, J = 8.1 Hz), 6.82

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(2H, d, J = 8.1 Hz), 3.79 (3H, s), 3.76 (1H, t, J = 7.3 Hz), 3.72−3.65 (1H, m), 3.64−3.56 (1H, m), 2.59 (1H, sext, J = 7.3 Hz), 2.54 (2H, t, J = 7.3 Hz), 2.35−2.26 (1H, m), 1.97−1.87 (1H, m), 1.70−1.62 (1H, m), 1.62−1.44 (2H, m), 1.44−1.34 (1H, m), 1.32−1.21 (1H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.6, 134.8, 129.2, 113.6, 75.4, 62.9, 55.2, 37.9, 35.0, 33.6, 30.5, 29.6, 27.0, 25.9, 23.4; IR (NaCl, cm^{-1}) 2932, 2851, 1613, 1512, 1246, 1111, 1038, 827; MS (rel int) m/z 260 (M^+, 1), 176 (65), 134 (100), 121 (66), 84 (37), 69 (9); HRMS calcd for $C_{17}H_{24}O_2$ 260.1776 (M + H, 261.1855), found 261.1866.

*8-[3-(4-Methoxyphenyl)propyl]-2-oxabicyclo[4.2.0]octane (**10b**) (cis, minor):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.10 (2H, d, J = 8.1 Hz), 6.82 (2H, d, J = 8.1 Hz), 4.09 (1H, q, J = 4.4 Hz), 3.87−3.81 (1H, m), 3.79 (3H, s), 3.18 (1H, t, J = 11.0 Hz), 2.61−2.45 (2H, m), 2.20−2.12 (1H, m), 2.12−2.04 (1H, m), 1.94−1.82 (2H, m), 1.82−1.72 (1H, m), 1.56−1.46 (5H, m), 1.44−1.37 (2H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.5, 135.2, 129.2, 113.6, 75.3, 64.6, 55.2, 37.8, 35.2, 30.5, 29.7, 29.1, 28.1, 23.5, 21.8; IR (NaCl, cm^{-1}) 2929, 2853, 1613, 1512, 1246, 1177, 1040, 828; MS (rel int) m/z 260 (M^+, 1), 176 (46), 134 (100), 121 (74), 84 (27), 69 (7); HRMS calcd for $C_{17}H_{24}O_2$ 260.1776 (M + H 261.1855), found 261.1871.

*8-(4-Methoxy-2-methylbenzyl)-2-oxabicyclo[4.2.0]octane (**13a**) (trans, major):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.03 (1H, d, J = 8.2 Hz), 6.71 (1H, d, J = 1.4 Hz), 6.68 (1H, dd, J = 8.2, 1.4 Hz), 3.87 (1H, t, J = 6.4 Hz), 3.78 (3H, s), 3.71 (1H, t, J = 8.8 Hz), 3.64−3.58 (1H, m), 2.91−2.80 (2H, m), 2.57 (1H, dd, J = 13.9, 8.1 Hz), 2.42−2.34 (1H, m), 2.28 (3H, s), 1.97−1.88 (1H, m), 1.75−1.68 (1H, m), 1.57−1.46 (3H, m), 1.39 (1H, dt, J = 11.0, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.7, 137.3, 131,1, 129.7, 115.8, 110.8, 74.7, 63.0, 55.2, 38.1, 35.8, 30.5, 26.9, 25.7, 23.3, 19.8; IR (NaCl, cm^{-1}) 2936, 2858, 1609, 1502, 1254, 1112, 1052, 863; MS (rel int) m/z 246 (M^+, 2), 162 (100), 147 (48), 135 (13), 91 (12), 55 (5); HRMS calcd for $C_{17}H_{24}O_2$ 246.1620 (M + H 247.1698), found 247.1687.

*8-(4-Methoxy-2-methylbenzyl)-2-oxabicyclo[4.2.0]octane (**13b**) (cis, minor):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.08 (1H, d, J = 8.8 Hz), 6.69 (1H, d, J = 2.1 Hz), 6.66 (1H, dd, J = 8.8, 2.1 Hz), 4.12 (1H, q, J = 4.4 Hz), 3.95−3.86 (1H, m), 3.76 (3H, s), 3.21 (1H, t, J = 11.0 Hz), 2.78 (1H, dd, J = 13.9, 7.3 Hz), 2.57 (1H, dd, J = 13.9, 8.1 Hz), 2.39−2.25 (4H, m), 2.23−2.11 (1H, m), 2.01 (1H, q, J = 10.3 Hz), 1.95−1.86 (1H, m), 1.86−1.77 (1H, m), 1.65−1.50 (2H, m), 1.49−1.39 (1H, m); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 158.5, 137.7, 133.8, 130.7, 115.1, 110.7, 75.2, 64.7, 55.2, 38.0, 30.3, 29.7, 29.3, 23.4, 21.8, 20.1; IR (NaCl, cm^{-1}) 2918, 2850, 2359, 1608, 1489, 1289, 1239, 1050; MS (rel int) m/z 246 (M^+, 3), 162 (100), 147 (63), 135 (18), 91 (19), 55 (8); HRMS calcd for $C_{17}H_{24}O_2$ 246.1620 (M + H 247.1698), found 247.1673.

*8-(4-Phenoxybenzyl)-2-oxabicyclo[4.2.0]octane (**14a**) (trans, major):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.40−7.29 (2H, m), 7.13 (2H, d, J = 8.1 Hz), 7.07 (1H, t, J = 7.3 Hz), 6.99 (2H, d, J = 8.8 Hz), 6.96−6.89 (2H, m), 3.89 (1H, t, J = 6.6 Hz), 3.78−3.67 (1H, m), 3.66−3.55 (1H, m), 2.96−2.81 (2H, m), 2.73−2.58 (1H, m), 2.47−2.31 (1H, m), 2.04−1.87 (1H, m), 1.79−1.66 (1H, m), 1.60−1.46 (2H, m), 1.40 (1H, dt, J = 11.0, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.6, 155.1, 135.8, 129.8, 129.6, 122.9, 118.5, 74.7, 63.0, 39.2, 39.0, 30.5, 26.9, 25.7, 23.3; IR (NaCl, cm^{-1}) 3302, 2935, 2851, 1592, 1505, 1238, 1108, 868; MS (rel int) m/z 294 (M^+, 1), 210 (11), 117 (28), 91 (21), 77 (100), 51 (39); HRMS calcd for $C_{20}H_{22}O_2$ 294.1620 (M + H 295.1698), found 295.1718.

*8-(4-Methylbenzyl)-2-oxabicyclo[4.2.0]octane (**20a**) (trans, major):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.07 (4H, dd, J = 11.0, 8.7 Hz), 3.87 (1H, t, J = 6.4 Hz), 3.77−3.64 (1H, m), 3.64−3.52 (1H, m), 2.98−2.73 (2H, m), 2.60 (1H, dt, J = 10.5, 5.0 Hz), 2.42−2.32 (1H, m), 2.31 (3H, s), 2.00−1.83 (1H, m), 1.72−1.62 (1H, m), 1.54−1.43 (2H, m), 1.39 (1H, dt, J = 11.0, 7.3 Hz), 1.26 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.7, 135.1, 128.9, 128.4, 74.7, 63.0, 39.3, 39.2, 30.4, 26.8, 25.7, 23.3, 21.0; IR (NaCl, cm^{-1}) 2933, 2849, 2362, 1516, 1452, 1220, 1108, 1056; MS (rel int) m/z 216 (M^+, 1), 132 (19), 117 (34), 105 (10), 84 (100), 55 (13); HRMS calcd for $C_{15}H_{20}O$ 216.1514 (M + H 217.1592), found 217.1601.

*8-(2,4-Dimethylbenzyl)-2-oxabicyclo[4.2.0]octane (**21a**) (trans, major):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.00 (1H, d, J = 8.1 Hz), 6.96 (1H, s), 6.93 (1H, d, J = 8.1 Hz), 3.87 (1H, t, J = 6.6 Hz), 3.78−3.67 (1H, m), 3.66−3.60 (1H, m), 2.95−2.82 (2H, m), 2.68−2.55 (1H, m), 2.44−2.35 (1H, m), 2.28 (3H, s), 2.26 (3H, s), 2.00−1.86 (1H, m), 1.78−1.67 (1H, m), 1.62−1.45 (3H, m), 1.39 (1H, dt, J = 11.0, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.8, 135.8, 135.3, 130.9, 128.8, 126.4, 74.7, 63.0, 37.9, 36.2, 30.5, 27.0, 25.7, 23.3, 20.9, 19.5; IR (NaCl, cm^{-1}) 3294, 2937, 2860, 2358, 1505, 1451, 1218, 1112; MS (rel int) m/z 230 (M^+, 1), 146 (66), 131 (100), 115 (24), 84 (55), 71 (76); HRMS calcd for $C_{16}H_{22}O$ 230.1671 (M + H 231.1749), found 231.1722.

*8-(2,4-Dimethylbenzyl)-2-oxabicyclo[4.2.0]octane (**21b**) (cis, minor):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.05 (1H, d, J = 7.3 Hz), 6.94 (1H, s), 6.91 (1H, d, J = 7.3 Hz), 4.13 (1H, q, J = 4.4 Hz), 3.97−3.85 (1H, m), 3.21 (1H, t, J = 11.0 Hz), 2.80 (1H, dd, J = 13.9, 7.3 Hz), 2.60 (1H, dd, J = 13.9, 7.3 Hz), 2.39−2.28 (1H, m), 2.27 (6H, s), 2.21−2.10 (1H, m), 2.02 (1H, q, J = 10.3 Hz), 1.97−1.86 (1H, m), 1.86−1.75 (1H, m), 1.55−1.50 (1H, m), 1.49−1.39 (1H, m), 1.26 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.7, 135.8, 134.9, 130.8, 128.8, 126.3, 75.3, 64.6, 37.9, 31.1, 30.3, 29.4, 23.5, 21.8, 20.9, 19.4; IR (NaCl, cm^{-1}) 2923, 2854, 2361, 1505, 1449, 1071, 1046, 829; MS (rel int) m/z 230 (M^+, 1), 146 (78), 131 (100), 119 (4), 84 (44), 55 (7); HRMS calcd for $C_{16}H_{22}O$ 230.1671 (M + H 231.1749), found 231.1742.

*8-(2,4,6-Trimethylbenzyl)-2-oxabicyclo[4.2.0]octane (**22a**) (trans, major):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.83 (2H, s), 3.86 (1H, t, J = 7.3 Hz), 3.71−3.58 (1H, m), 2.92−2.77 (2H, m), 2.71 (1H, dd, J = 14.7, 9.6 Hz), 2.40−2.31 (1H, m), 2.28 (6H, s), 2.24 (3H, s), 2.00−1.83 (1H, m), 1.70−1.58 (1H, m), 1.55−1.42 (2H, m), 1.38 (1H, dt, J = 10.5, 7.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.2, 134.9, 134.9, 128.9, 74.3, 62.8, 38.1, 32.1, 30.7, 27.2, 25.6, 23.5, 20.8, 20.3; IR (NaCl, cm^{-1}) 2937, 2861, 2359, 1455, 1375, 1216, 1103, 852; MS (rel int) m/z 244 (M^+, 1), 160 (71), 145 (100), 133 (13), 84 (20), 55 (15); HRMS calcd for $C_{17}H_{24}O$ 244.1827 (M + H 245.1905), found 245.1911.

*8-(2,4,6-Trimethylbenzyl)-2-oxabicyclo[4.2.0]octane (**22b**) (cis, minor):* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.81 (2H, m), 4.11 (1H, q, J = 3.7 Hz), 3.96−3.86 (1H, m), 3.28−3.17 (1H, m), 2.90−2.77 (1H, m), 2.77−2.67 (1H, m), 2.30 (6H, s), 2.28 (1H, s), 2.24 (1H, s), 2.23 (3H, s), 2.17−2.06 (2H, m), 1.96−1.79 (2H, m), 1.60−1.49 (1H, m), 1.49−1.41 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 136.4, 135.9, 134.6, 128.7, 76.0, 64.7, 38.2, 30.6, 30.1, 27.7, 23.4, 21.7, 20.8, 20.2; IR (NaCl, cm^{-1}) 2923, 2858, 2361, 2343, 1449, 1064, 1049, 850; MS (rel int) m/z 244 (M^+, 1), 160 (61), 145 (100), 133 (13), 84 (11), 71 (99); HRMS calcd for $C_{17}H_{24}O$ 244.1827 (M + H 245.1905), found 245.1918

*1-(2-Ethoxy-3-methylcyclobutylmethyl)-4-methoxybenzene (**27**):* ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.07 (2H, d, J = 8.1 Hz), 6.81 (2H, d, J = 8.1 Hz), 3.78 (3H, s), 3.43 (2H, m), 3.16 (1H, t, J = 7.3 Hz), 2.88 (1H, dd, J = 13.9, 5.1 Hz) 2.55 (1H, dd, J = 13.9, 9.5 Hz), 2.22 (1H, m), 2.02 (1H, sept, J = 7.3 Hz) 1.94 (1H, dd, J = 14.7, 8.7 Hz), 1.17 (3H, t, J = 7.3 Hz), 1.10 (3H, d, J = 6.6 Hz), 0.77 (1H, dd, J = 14.7, 10.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 157.7, 132.8, 129.5, 113.6, 85.5, 64.1, 55.2, 42.1, 40.1, 35.7, 27.0, 19.8, 15.5; IR (NaCl, cm^{-1}) 2952, 2930, 2867, 1512, 1245, 1177, 1119, 1038; MS (rel int) m/z 234 (M^+, 5), 192 (66), 148 (100), 121 (90), 91 (48), 77 (54); HRMS calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1630.

■ ASSOCIATED CONTENT

Supporting Information. Additional schemes and figures, coordinates, general information, experimental details,

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characterization data, and copies of ^{1}H NMR and ^{13}C NMR spectra of new compounds This material is available free of charge via the Internet at http://pubs.acs.org.

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