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Efficient electrocatalytic intramolecular anion radical cyclobutanation reactions

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Abstract—Electrochemically initiated, intramolecular anion radical cyclobutanations of bis(enones) and related substrates are presented. The formation of novel anion radical Diels–Alder adducts in minor amounts is also observed. Total yields of pericyclic products, which include both *cis*- and *trans*-cyclobutanes and a single Diels–Alder adduct, are generally high (51–88%), with electrocatalytic factors in the range of 1.5–5. Mechanistically, strong evidence for the intervention of distonic anion radical intermediates as precursors of both types of pericyclic products is presented. The scope and limitations of these reactions are rather extensively explored and defined, and in particular the tendency, in some cases, for electrogenerated base-catalyzed reactions to compete with these anion radical pericyclic reactions.

1. Introduction

Cyclobutanation reactions of the cation radicals of alkenes with neutral alkenes have by now become rather commonplace and are characterized by impressively high cycloaddition rates and low activation barriers, especially in comparison to the corresponding thermal reactions.[1,2] There have been some recent indications that this extensive body of cation radical cyclobutanation chemistry may have a close counterpart in the domain of anion radical chemistry. Specifically, the reduction of phenyl vinyl sulfone under electrochemical conditions (mercury pool cathode) has been reported to yield *trans*-1,2-bis(phenylsulfonyl)cyclobutane.[3] Subsequently, the cyclodimerizations of a variety vinylpyridines and vinylquinolines under similar conditions have also been established.[4] Still more recently, a few intramolecular anion radical cyclobutanations of tethered bis(enones) have been described from these laboratories.[5,6] These anion radical reactions are of special interest because they represent rare examples of intramolecular anion radical cycloaddition, rather than the more common electrohydrocyclization/dimerization (EHC or EHD).[7,8]

The environmentally benign nature of these electrochemical conversions, inherent in the simplified workup and the consumption of electricity as the sole reagent (in catalytic amounts), further add to their experimental appeal and potential utility. The present paper reports the development of substantially more efficient conditions than those previously reported for carrying out these electrocatalytic intramolecular cycloaddition reactions in high yields, and further extends the scope and defines the limitations of these reactions. In particular, the use of tetraalkylammonium tetrafluoroborates as electrolytes in acetonitrile solution is developed as a particularly efficient method for these cyclobutanations. From a mechanistic viewpoint, experiments are described which strongly support the formulation of the cycloaddition reaction as proceeding in a stepwise fashion, via a distonic anion radical intermediate. Other new mechanistic and theoretical aspects of the reaction are clarified, including the requirement of at least one aroyl group, and the preference for two aroyl moieties.

2. Results and discussion

2.1. Electrolysis of 1a

The cyclobutanations of substrates **1a** and **1g** (Scheme 1) have previously been reported from these laboratories. Using lithium perchlorate (0.1 M) as the electrolyte, the reaction of **1a** was found to afford a total yield of pericyclic products (**2**, **3**) of just 45%, and the ratio of *trans*-**2**/*cis*-**2**/**3** was found to be 2.4:2.0:1. The total yield of pericyclic products obtained from **1g** was even smaller (35%).[5] Consequently, various electrolytes (and other procedural changes) were investigated in the present work in order to determine whether synthetically useful procedures might be developed for carrying out these novel reactions.

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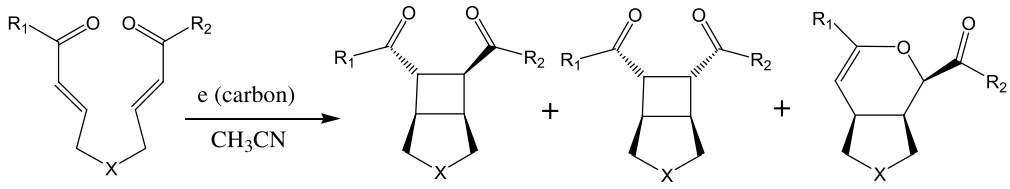


	X	$R_1 = R_2$		X	R_1	R_2
1a	CH_2	Ph	**1f**	CH_2	4-Ph-Ph	4-Ph-Ph
1b	O	Ph	**1g**	CH_2	Ph	CH_3
1c	CH_2	4-Cl-Ph	**1h**	CH_2	CH_3	CH_3
1d	CH_2	3,4-Cl_2-Ph	**1i**	CH_2	Ph	OEt
1e	CH_2	2-Naphthyl	**1j**	CH_2	OEt	OEt

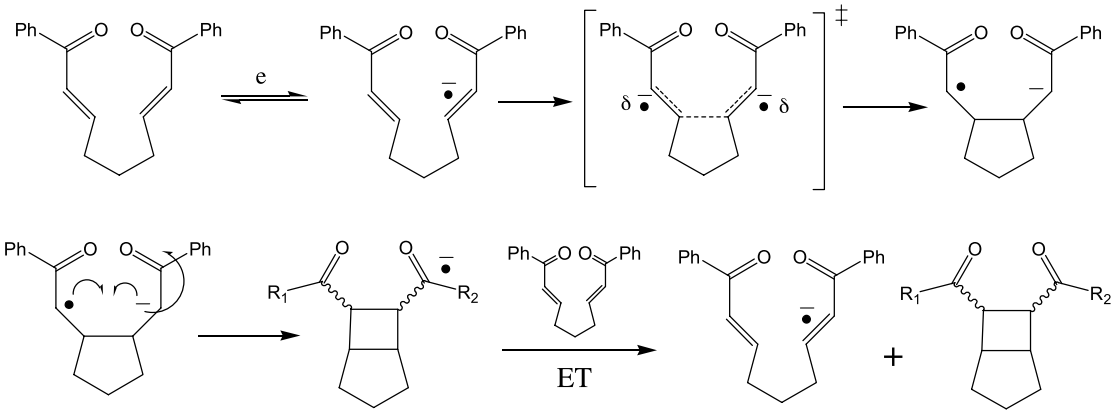
Scheme 1. Pericyclic products in the electrocatalytic, intramolecular anion radical cyclobutanation reactions of various bis(enones).

2.1.1. The anion radical mechanism. The anion radical chain cycloaddition mechanism proposed for these reactions is rather novel and is summarized in Scheme 2. According to this mechanism, reduction of the substrate at the cathode leads to a substrate anion radical, which then cyclizes to a distonic anion radical intermediate. This intermediate cyclizes to the anion radical of the cyclobutane product. The anion radical moiety presumably resides upon one of the benzoyl groups. Finally, exergonic electron transfer (ET) from the product anion radical to a molecule of the neutral substrate occurs, setting up the chain process and affording the neutral cyclobutane product. The distonic anion radical intermediate can also cyclize to a Diels–Alder adduct anion radical, where the anion radical moiety again resides upon a benzoyl moiety.

2.1.2. Tetraalkylammonium tetrafluoroborate electrolytes. The use of tetraalkylammonium tetrafluoroborates as electrolytes was explored on the assumption that ion pairing to the tetraalkylammonium cation should be much looser than with the lithium ion, resulting in a possible increase in reactivity of the anion radical intermediates. In fact, in the case of **1a**, a dramatic increase in yield to 88% was observed under these conditions. As will be noted in Table 1, the yield of the *trans* cyclobutane product (*trans*-**2**) is elevated to 59%. Since the *cis* isomer (obtained in 17% yield) is readily isomerized to the *trans* isomer under acidic or basic conditions, this reaction sequence makes the *trans* isomer available in an overall 71% yield. The novel Diels–Alder product (**3**), obtained in 13% yield, is also of inherent interest in that it represents the first documented instance of an anion radical Diels–Alder reaction. Since complete conversion of **1a** to products is accomplished after a maximum[9] of 21% of the theoretical charge had flowed, the reaction is mildly electrocatalytic, with a catalytic factor of 4.7 (representing a 0.21 F mol^{-1} process).

2.2. Electrolysis of 1b

2.2.1. Effect of electrogenerated bases. The extension of this chemistry to the ethereal substrate **1b** was investigated next. Under conditions similar to the earlier work (using lithium perchlorate as the electrolyte)[5] a total yield of 43% of pericyclic products was isolated, with *trans*-**2b** being the major product. Under both the present and former conditions the catalytic factor was <3. When tetrabutylammonium tetrafluoroborate was used as the electrolyte, pericyclics were isolated in 53% yield. Interestingly, this reaction proceeded somewhat more efficiently in terms of the catalytic factor (10.6) than any of the other reactions, but the yield of pericyclic products was diminished in comparison to the corresponding reduction of substrate **1a** when using the same electrolyte because of a competing reaction of the substrate (Scheme 3). The formation of **4b** implies a base catalyzed deprotonation of **1b**, followed by a Michael type addition of the conjugate base via the alpha carbon of the extended enolate to the beta carbon of the enone moiety. Formation of this product in the reaction using tetrabutylammonium tetrafluoroborate as the electrolyte, and not with any of the other electrolytes, is in



Scheme 2. Proposed mechanism for the anion radical chain cyclobutanation reaction of 1,7-dibenzoyl-1,6-heptadiene.

Table 1. Yields and catalytic factors for the electrocatalytic intramolecular anion radical pericyclic reactions of various bis(enone) substrates (**1**)

Substrate	Procedure[a]	Yield of *trans*-**2**	Yield of *cis*-**2**	Yield of **3**	Total pericyclic yield	Other products	Catalytic factor
1a	A	59%	17%	13%	88%	—	4.7
1b	A	39	11	3	53	**4b**; 11%	10.6
1b	B	21	20	2.0	43	—	1.6
1b	C	21	39	28	88	—	1.8
1c	A	52	11	12	75	**5c**; 5%	5.1
1d	B+C	7	33	16	56	**6d**; 6%	1.3
1d	D	3	0	0	3	**5d**; 17%[b]	7.3
1e	A	29	14	8	51	**5e**; 17%	5.2
1f	C	7	21	25	53	**5f**; 13%, **7f**; 7%	1.9
1f	A	12	0	0	12	**5f**; 17%	1.4
1g	C	0	9	0	9	**7g**; 30%[c]	<1
1g	D	19[d]	0	0	19	—	1.8
1i	B	32[e]	0	0	32	—	<1
1j	D	0	0	0	0	**5j**; 42%	4.5

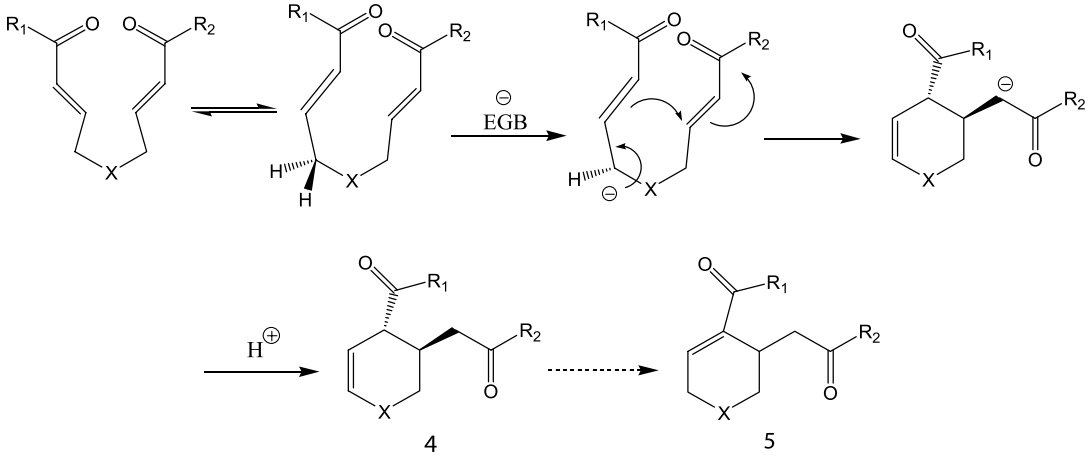
[a] The electrolytes used in the respective procedures were: A=0.1 M tetrabutylammonium tetrafluoroborate; B=0.1 M lithium perchlorate; C=0.1 M magnesium perchlorate; D=0.1 M tetraethylammonium tetrafluoroborate.
[b] Also obtained 35% of an unidentified polymer.
[c] Two isomers.
[d] Both *trans* isomers were observed: 12 and 7% (~2:1 ratio), X-ray of major isomer provided.
[e] Both *trans* isomers were observed: 28 and 4% (7:1 ratio).

agreement with the postulate that the intermediate anionic species are less tightly ion paired under these conditions, and are therefore substantially more reactive (basic). Since a product analogous to **4b** was not observed in the electrochemical reaction of **1a**, it is apparent that the substitution of oxygen for carbon tends to acidify the adjacent C–H bond. A similar competition has been reported in the EHC of butenolides.[10] In the case of substrate **1b**, a product corresponding to the isomerization of the double bond, into conjugation with the carbonyl group, was not observed. However, in several other instances products corresponding to such a structure, **5**,[11] were obtained instead of **4**. The nature of the electrogenerated base (EGB)[12,13] species responsible for the deprotonation is unknown, but likely candidates might be a substrate or product anion radical or a dianionic intermediate produced by further reduction of the proposed distonic anion radical intermediate.

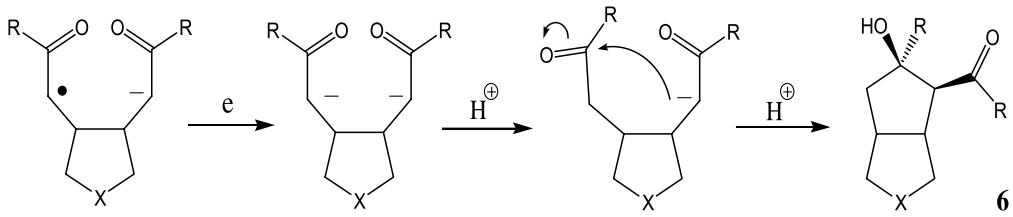
2.2.2. Use of $Mg(ClO_4)_2$ electrolyte. Although the use of tetraalkylammonium tetrafluoroborates as the electrolyte appears to be the more general method of choice for carrying out most of these anion radical cycloadditions with optimal efficiency, in the specific case of **1b** the competing reaction described above tended to lower the yields of the pericyclic products. In view of that, it appeared worthwhile to investigate the effect of using a more strongly ion-pairing counterion than even the lithium ion, that is, the magnesium ion. When the electrochemical reaction was carried out in the presence of magnesium perchlorate as the electrolyte, an 88% yield of pericyclic products was obtained. The increase in the *cis*/*trans* ratio in the cyclobutane product may also reflect the stronger ion pairing between the magnesium ion and the anion radical moiety in the transition state for the final cyclization step (vide infra).

2.3. Electrolysis of 1c

It had been found in the previously reported work[5] that the introduction of electron donating substituents, such as 4-methoxy, onto the aryl ring of **1a** sharply inhibits cyclobutanation. It is presumed that this is the result, at least in part, of the inability of the distonic anion radical intermediate to cyclize to the product cyclobutane anion radical, which would require the anion radical moiety to



Scheme 3. The electrogenerated base (EGB) catalyzed products (**4** and **5**) obtained in the electrochemical reduction of substrates **1**, in the presence of tetraalkylammonium tetrafluoroborate as the electrolyte.



Scheme 4. Formation of an aldol-type side product (**6**), via reduction of the distonic anion radical to an enolate dianion.

reside in a higher energy SOMO (that of a 4-methoxybenzoyl moiety) than in the case of the unsubstituted substrate. Consequently, the facility of bis(enone) anion radical cyclobutanation of substrates that would provide a lower energy product anion radical SOMO was investigated. Substrate **1c**, which has electron withdrawing 4-chloro substituents on both of its benzoyl groups, was found to undergo smooth anion radical cycloaddition under the tetrabutylammonium tetrafluoroborate electrolyte conditions, affording a 75% yield of total pericyclics, of which 52% was the *trans* cyclobutane. It is of special interest that the chlorine substituent is retained in the product, even though the 4-chlorobenzoyl anion radical moiety was potentially susceptible to chloride ion loss. Presumably, electron transfer from the product anion radical to substrate is sufficiently rapid as to suppress the potential loss of chloride ion.

2.4. Electrolysis of 1d

The introduction of an even more strongly electron withdrawing *meta* chloro substituent into the substrate, in addition to the *para* chloro substituent, as in substrate **1d** would be expected to accelerate the rate of the second cyclization step even further by providing a lower energy SOMO for the product anion radical. However, the considerably increased stabilization of the substrate anion radical, and the expected shift in electron density in the SOMO from the alkene moiety to the now rather strongly electron-deficient aroyl ring could also be expected to have an adverse effect upon the rate of the first cyclization step. In accord with the latter idea, when **1d** is electrolytically reduced in the presence of the tetraethylammonium tetrafluoroborate electrolyte, the yield of pericyclic products falls precipitously to 3%, the main products consisting of a 17% yield of a base-catalyzed cyclization/isomerization product (**5d**) and an uncharacterized polymer (35%). However, in the presence of a mixed lithium perchlorate/magnesium perchlorate electrolyte, the desired pericyclic reactions are observed to occur with moderate efficiency, but the yields of the pericyclic products are lower than in the case of **1c**, and an aldol-type product (**6d**) is also formed. This latter product is considered to result from reduction of the intermediate distonic anion radical to a dianion, which subsequently is protonated and undergoes cyclization (Scheme 4).

2.5. Electrolysis of 1e

The replacement of the phenyl group with a β-naphthyl or 4-biphenylyl group could also provide a more suitable venue for the stabilization of the anion radical of the product than in the case of **1a**, but again the lowering of the SOMO energy and the shifting of the SOMO density toward the aroyl moiety could retard the first cyclization step. The cyclobutanation of substrate **1e** (which has β-naphthyl substituents), using tetrabutylammonium tetrafluoroborate as the electrolyte, was found to proceed, albeit in moderate yield (51%), suggesting that the predominant effect of the increased delocalization provided by the naphthyl group is the lowering of the SOMO energy and the shift in density away from the alkene linkage. However, the retardation of the cyclization is evidently much less than in the case of the dichloro substrate **1d**. As in this latter case, the base-catalyzed cyclization/isomerization product **5e** was also formed (17%; Table 2). It is worth noting that when the reaction is not run to completion (~80% complete), the yield of pericyclic products is relatively unchanged, but the amount of the base catalyzed product is greatly reduced. This may well be indicative of a build up of electrogenerated bases within the solution, accelerating the cyclization to **5** in the latter stages of the reaction. This build up of base could also provide an explanation for the increase in the *trans*/*cis* ratio observed in the more complete reaction (vide infra).

2.6. Electrolysis of 1f

Substrate **1f**, which contains 4-biphenylyl moieties, responds in a manner rather similar to that of **1d**. Limited *trans*-**2f** formation is observed, along with greater formation of the base-catalyzed cyclization/isomerization product **5f** (tetraalkylammonium electrolyte). However the use of $Mg(ClO_4)_2$ afforded a moderate pericyclic yield of 53%. Substrate **1f** has limited solubility in acetonitrile, so that these reductions were carried out in 1:1 THF/acetonitrile solutions.

Table 2. The effect of the extent of reaction upon the yields of anion radical and base-catalyzed products

Substrate[a]	Yield of *trans*-**2**	Yield of *cis*-**2**	Yield of **3**	Total pericyclic yield	Other products	Catalytic factor
1e	29	14	8	51	**5e**; 17%	5.2
1e[b]	17	21	10	48	**5e**; 6%	5.4

[a] The electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate.
[b] Reaction run to 79% completion (based upon recovered **1e**), yields and catalytic factor are corrected for **1e** recovery.

2.7. SOMO requirements for cyclization

2.7.1. Electrolysis of 1g and 1h. In contrast to the aroyl groups considered above, acetyl groups provide a much less extensively delocalized, higher energy SOMO for the product cyclobutane or Diels–Alder anion radical. The potential anion radical pericyclic chemistry of substrate **1h**, which has two acetyl substitutents, was therefore not expected to be as efficient as when aroyl groups are present. In accord with this supposition, no pericyclic products at all could be detected in the electroreduction of this substrate.

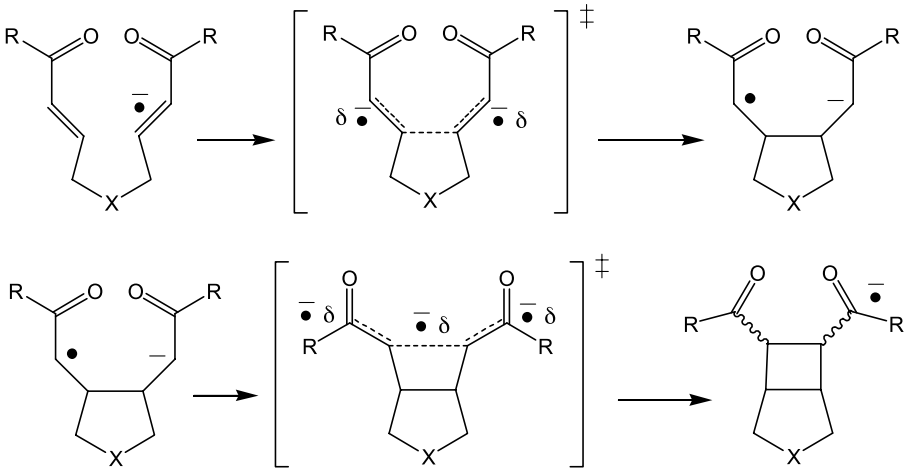
However, since the anion radical of the pericyclic products only requires (and perhaps can only utilize) a single aroyl moiety, it was considered likely that pericyclic chemistry might occur with unsymmetrical substrate **1g**, which has one benzoyl and one acetyl substituent. The previously reported results, using lithium perchlorate as an electrolyte, have already confirmed this conjecture, but further experiments were carried out in the present work in connection with magnesium perchlorate and tetraethylammonium tetrafluoroborate as the electrolytes. The observed yields in both cases are quite modest. However, an additional feature of interest emerges when tetraethylammonium tetrafluoroborate is used as the electrolyte, namely, that both possible *trans*-**2g** isomers are formed, in a 2:1 ratio, with the major cyclobutane having the benzoyl group *syn* to the cyclopentane ring.

2.7.2. Electrolysis of 1i. The reduction of **1i**, which has one benzoyl and one carboethoxy substituent, provides a still further example of the relative inefficiency of pericyclic chemistry when only a single benzoyl group is present. When electrolyzed in the presence of lithium perchlorate, **1i** provides a 32% yield of two isomers of *trans*-**2i**. The major isomer appears, on the basis of NMR comparisons, to be structurally analogous to the major *trans*-**2g** isomer obtained from **1g**. This reduction is unusual in that it is not catalytic. An intriguing possible interpretation of this data is that while benzoyl reduction is occurring readily and reversibly, the initial cyclization step is sharply retarded by the ineffectiveness of the ester function at delocalizing and stabilizing the SOMO in the transition state. This could require cyclization to occur via the rarer reduction of the unsaturated ester function. This higher energy anion radical could then rapidly cyclize to the reactive benzoyl ene function. The key factor here is that catalysis would necessarily involve electron transfer from a product anion radical to a substrate molecule, and this chemical electron transfer undoubtedly is highly selective for formation of the more stable, and apparently unreactive, anion radical corresponding to the benzoyl enone function. Additionally, this chemical electron transfer is likely to be irreversible in nature, halting catalysis. The chemically reduced substrate may prove reactive in non-cyclobutanation mechanisms, which may account for the observed low yield.

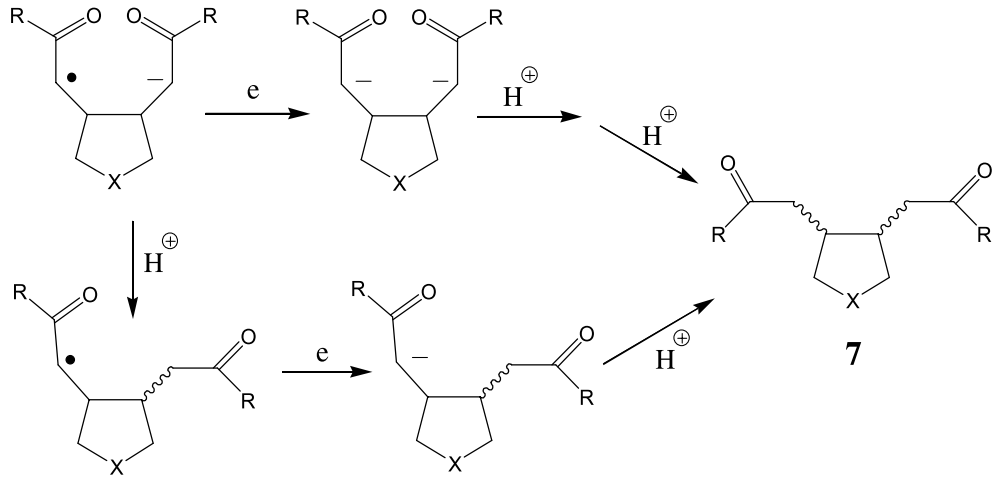
2.7.3. Diminished cyclization rates. Since the desired pericylic reaction products provide the required low energy SOMO associated with an aroyl function (in this case, benzoyl), and the starting substrate provides a readily reducible aroyl enone function, it appears likely that the lower efficiency of the desired pericyclic chemistry in the substrates which contain only a single aroyl function must arise from diminished cyclization rates in either one or both of the cyclization steps. It therefore seems reasonable to propose that, in the transition states for both cyclization steps, the SOMO is at least partially delocalized over both enone moieties, as indicated in Scheme 5. The delocalization is presumably greatest, and the SOMO energy the lowest, when both keto functions are of the aroyl type.

2.8. Evidence for the distonic anion radical intermediate

In most cases the electrolyte systems (lithium/magnesium perchlorate or tetraalkylammonium tetrafluoroborate) lead to the formation of a mixture of the *cis* and *trans* cyclobutane isomers. At the earliest point of the electrochemical reactions at which these products could be detected, the *trans* cyclobutane was always formed in modest excess over the *cis* isomer. As the reaction progressed further toward completion, the *trans*/*cis* ratio progressively increased. The values given in Table 1 correspond to reactions run essentially to completion. This progressive change in the *trans*/*cis* ratio suggested the possibility that a portion of the *cis* isomer was being isomerized to the more stable *trans* isomer in the course of the reaction. Although a base-catalyzed isomerization was



Scheme 5. Proposed delocalization of the SOMO over both carbonyl groups in the transition states for both cyclization steps.



Scheme 6. Mechanism of formation of **7**, via protonation of distonic intermediate.

formally a possibility, it also appeared possible that anion radicals of the *cis*-cyclobutane were being reformed during the reaction and subsequently reverting to the distonic anion radical, which could once again cyclize to give either cyclobutane isomer or the Diels–Alder adduct. A distinction between these two mechanistic possibilities is therefore possible, based upon the predicted formation of small amounts of the Diels–Alder adduct in the latter mechanism. To test this possibility, isomers of **2b** were isolated and used in electrolysis reactions with lithium perchlorate as the electrolyte. A quantity of *cis*-**2b** was reduced in isolation, leading to the formation of *trans*-**2b** (32%), **3b** (7%), an aldol product **6b** (11%), a dihydrocyclopentane product **7b** (20%; see Scheme 6), with a further 18% of unreacted *cis*-**2b**. The attempted reduction of *trans*-**2b**, as expected, failed to lead to any reaction. A degree of reactivity was seen under extreme conditions (very negative potentials, large amounts of charge). Although some *trans*-**2b** was still returned, no other known products were obtained. This clearly indicates that, while the *trans* isomer is stable toward continued reduction at normal potentials, the *cis* isomer readily reverts to the proposed distonic intermediate. This not only allows for the formation of the *trans* and Diels–Alder products, but also of **7b**, which represents protonation after the first cyclization, effectively 'trapping' the distonic anion. In further accord with the postulate of *cis–trans* isomerization via regeneration of the distonic anion radical intermediate is the previously discussed absence of any base-catalyzed products (e.g., **4** and **5**) in any perchlorate reaction system. Since the distonic anion radical intermediate is evidently involved in the reversal of the cycloaddition, an application of the law of microscopic reversibility strongly suggests that the forward reaction also involves the same distonic intermediate.

2.9. Trapping of the distonic anion radical intermediate/inhibition of EGB pathway

It was thought that addition of a slight excess of a weak acid would not only inhibit EGB pathways but would also trap (protonate) the proposed distonic anion radical. Indeed this was realized with a 1.6 M excess of acetic acid placed in the solution from the beginning of electrolysis. The naphthoyl substrate **1e** was chosen as it leads to modest base-catalyzed product formation (17% of **5e**). The expected trapping is clearly the dominant mechanism, represented by both **6e** and **7e** formation (Table 3). The expected reduction in base-catalysis (product **5e**) is also seen, down to just 3%. Also, by limiting the excess of acetic acid, we were still able to obtain small amounts of our primary cyclobutanation product (*trans*-**2e**), although formation of *cis*-**2e** and **3e** were reduced to levels below detection. The proposed mechanism for the formation of **7** is given in Scheme 6.

2.10. Mediated electrolysis

The possibility of developing a mediated electrochemical reduction method was also probed. The strategy adopted was to provide a mediator which is (in the ideal case, selectively) reduced at a less negative potential than the substrate, and which forms a relatively long-lived anion radical capable of mildly endergonic electron transfer to the substrate molecules.[14–16] This strategy should provide for a low substrate anion radical concentration, which could minimize anion radical to anion radical coupling as well as over-reduction of the substrate (dianion formation). Initial attempts utilized **1b** as the substrate and magnesium or lithium perchlorate as the electrolyte. Benzil (diphenyl diketone), dypnone (*E*-3-phenyl-2-butenoylbenzene), and benzophenone were investigated as mediators, but all three

Table 3. Effect of a weak acid in solution during electrolysis of **1e**

Additive	% Yield of *trans*-**2e**	% Yield of *cis*-**2e**	% Yield of **3e**	% Yield of **5e**	% Yield of **6e**	% Yield of **7e**	% Yield of products
None	29	14	8	17	0	0	68
1.6 M excess of acetic acid	6	0	0	3	14	38	61

Table 4. Anion radical versus base-catalyzed reactions in the mediated electrolysis of **1c**

Mediator	% Yield of *trans*-**2c**	% Yield of *cis*-**2c**	% Yield of **3c**	% Yield of **5c**
None	52	11	12	5
Benzophenone	42	11	7	13
Benzil	0	0	0	28[a]

[a] Along with 42% unidentified polymer.

proved to be ineffective. Mediator reduction did occur at less negative potentials (as evidenced by a temporary solution color change) than that of the substrate, but products did not form until the potential was reduced to the usual value for reduction of the substrate.

Further studies were directed toward the use of tetraethylammonium tetrafluoroborate as the electrolyte, this time using **1c** as the substrate. Although these conditions failed to provide an increase in yield of pericyclic products, they did provide important insights into the interplay between anion radical cyclization and electrogenerated base catalysis (Table 4). Benzophenone reduction was found to occur at nearly the same potential as for **1c**, when benzil reduction occurred at a much less negative potential. In the case of benzil, this occurred at a potential that did not lead to substrate reduction, so no pericyclic products were formed. On the other hand, in the absence of a mediator, base-catalyzed products (such as **5c**) were formed in a low yield. When benzophenone was employed as the mediator, both types of products were formed, indicating that both the substrate and mediator are being reduced at the cathode. Apparently, anion radical cyclobutanation occurs only when the substrate is reduced, and reduction of the mediator leads essentially only to the base-catalyzed reaction. These observations indicate that the desired mildly endergonic electron transfer is too slow to compete with the base-catalyzed reactions.

2.11. Efficient base-catalyzed reactions

The observations noted above immediately suggested the possibility of employing an excess of benzil to engender a highly catalytic method for selectively and efficiently forming the base-catalyzed product. This possibility was realized in the case of the electrochemical reduction of **1b** in the presence of a relatively large excess of benzil, which gave only **4b**, in 68% yield. The catalytic factor here was rather modest at 2.8, although low concentrations of starting material and a large excess of benzil made judging the end of the reaction difficult. Comparison of this result with that obtained for **1c** (with benzil) suggests that the use of mediators to engender these base-catalyzed cyclizations may prove problematic, due to competition with polymerization. The efficiency seen with formation of **4b** may be engendered by the greater acidity of the protons (alpha to the bridging oxygen) in **1b**.

3. Conclusions

The present paper reports the development of conditions for carrying out electrochemically initiated, intramolecular anion radical cyclobutanations of bis(enones) and related substrates in high yields and with substantially less than the theoretical consumption of electricity (i.e., electrocatalytically). The solvent/electrolyte combination acetonitrile/tetraalkylammonium tetrafluoroborate is found to be an especially effective one for producing high yields and large catalytic factors. The formation of novel anion radical Diels–Alder adducts in minor amounts is also verified. The scope and limitations of these reactions are rather extensively explored and defined. In particular, the reactions have been found to have an absolute requirement for at least one aroyl ketone moiety and a significant preference for both ketonic moieties to be of the aroyl type. Theoretical rationales for these requirements and preferences are presented. Strongly electron-withdrawing substituents (upon the aroyl moiety) tend to decrease reaction efficiency by diminishing the rate of the first cyclization step, such that a competition between anion radical mediated and electrogenerated base-catalyzed reactions is observed. Evidence for a stepwise (as opposed to concerted) cycloaddition mechanism involving a distonic anion radical intermediate is presented, and the distonic anion intermediate has been trapped.

4. Experimental

4.1. General electrolysis procedure

A typical experiment utilizes 100 mg of a given bis(enone) substrate, which equates to 0.329 mmol for substrate **1a**. The substrate is dissolved in 22 mL of electrolyte solution, giving a typical substrate concentration of 0.0150 M, and added to the working electrode (WE) compartment of the electrolysis cell. The electrolyte solution is 0.100 M (unless stated) in either alkylammonium or perchlorate salt (detailed below) in dry acetonitrile (unless stated). The acetonitrile is distilled fresh for each electrolysis from a reservoir containing phosphorus pentoxide. Electrolyte solution (6 mL) is added to the counter electrode (CE) compartment.

Electrolysis of the substrate was carried out at specific voltages (detailed below) with stirring under positive nitrogen flow at room temperature. The voltage is commonly increased through the course of an electrolysis to help maintain the current (tracked by coulometer). This increase is detailed in the description of each electrolysis. Electrolysis voltages were versus a 'pseudo-standard' silver wire (encased in porous vycor glass) reference electrode (RE).[17] The RE used is seen to have a calibration to SCE of approximately $+0.1$ V, when in 0.1 M Et_4NBF_4 acetonitrile solution. The CE and WE consisted of reticulated vitreous carbon (25 mm$\times$5 mm$\times$5 mm), their corresponding compartments separated by a course frit. The RE was placed within 0.5 cm of the WE. The reaction was stopped when thin-layer chromatography (TLC) indicated that the starting

material had been consumed. The reactant solution (WE compartment only) then underwent an aqueous workup with sequential benzene washings (alkyl ammonium salt) or dichloromethane (perchlorate salt). The organic phase was retained and dried with Na_2SO_4. The benzene/dichloromethane was removed by rotary evaporation, with the crude solution being purified by preparative TLC (1 mm thick, elution with ethyl acetate/petroleum ether mixture, 1:9 ratio, unless stated). Bands were identified, collected by scraping, and extracted with dichloromethane. Filtering removed the silica, with a rotary evaporator again employed to remove the solvent, yielding the desired products.

Notes. In cases when starting material is recovered, the yields of products and the catalytic factors are corrected accordingly. Characterization of products is in most cases completed by comparison to the products obtained from **1b** electrolysis, and to results previously published (as referenced). The products from **1b** are more fully characterized both by 500 MHz NMR ($^1H/^{13}C$) and HRMS. Their ready crystallization also allowed for X-ray structural determination (provided previously[6]). All novel products are also characterized by HRMS or, in two cases, by X-ray crystallography.

4.2. Analysis

Room temperature ^1H NMR spectra were recorded on a Varian Unity+300 as solutions in $CDCl_3$. ^{13}C NMR and COSY spectra were recorded on a Varian Unity Inova 500 spectrometer. Chemical shifts (δ) are relative to tetramethylsilane, and coupling constants (J) are given in Hertz (Hz). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; br, broad. X-ray diffraction analyses were conducted using a Nonius Kappa CCD diffractometer. Low-resolution mass spectra (LRMS) were recorded on a Finnigan MAT TSQ-70 mass spectrometer, with high-resolution mass spectra (HRMS) recorded on a VGZAB-2E mass spectrometer.

4.3. Equipment/reagents

A potentiostatic controller, the Electrosynthesis Company (ESC) model 415, was used to control the applied potential. The charge used was tracked by a digital coulometer, ESC model 640. The applied potential was confirmed using a digital multimeter (Wavetek DM7), operating as a potentiometer. The electrode material was Duocel 80 PPI reticulated vitreous carbon. The substrates were kindly produced within the Krische group or by Dr. Jingkui Yang.[5,6] Reagent purity was assayed by NMR/LRMS. Electrolytes were used as purchased, from Alfa Aesar (98% purity).

4.4. Electrolysis of *E,E*-1,7-dibenzoyl-1,6-heptadiene (1a)

Electrolysis of 111 mg (0.0166 M) of **1a** with Bu_4NBF_4 electrolyte, at −2.0 V versus RE (first 3.0 C at −1.5 V). The reaction appeared complete after 7.5 C, or 21.3% (of required charge) had passed through the cell. PTLC purification of the 105 mg of recovered crude yielded *cis*-**2a** (19 mg, 17%), *trans*-**2a** (65 mg, 59%), and **3a** (14 mg, 13%) for a total of 98 mg of pericyclic products (88%). No starting material was recovered, and no other products were identified.

4.4.1. Compound *cis*-2a[5,6]. ^1H NMR (300 MHz, $CDCl_3$): 1.65 (2H, m), 1.84 (2H, m), 2.02 (2H, m), 3.20 (2H, br.s), 3.85 (2H, d, J=4.2 Hz), 7.35 (4H, br.t, J=7.2 Hz,), 7.44 (2H, br.t, J=7.2 Hz), 7.75 (2H, br.d, J=8.1 Hz).

4.4.2. Compound *trans*-2a[5,6]. ^1H NMR (300 MHz, $CDCl_3$): 1.42 (2H, m), 1.52 (1H, m), 1.85 (3H, br.m), 3.06 (1H, q, J=6.9 Hz), 3.24 (1H, m), 4.28 (1H, dd, J=6.6, 7.5 Hz), 4.57 (1H, dd, J=7.8, 10.5 Hz), 7.46 (4H, m), 7.55 (2H, m), 7.95 (2H, br.d, J=6.9 Hz), 8.02 (2H, br.d, J=7.2 Hz).

4.4.3. Compound 3a[5,6]. ^1H NMR (300 MHz, $CDCl_3$): 1.60 (2H, m), 1.84 (2H, m), 2.01 (2H, m), 2.69 (2H, m), 4.89 (1H, d, J=6.6 Hz), 5.59 (1H, d, J=3.0 Hz), 7.26 (3H, m), 7.48 (4H, m), 8.08 (2H, d, J=7.5 Hz).

4.5. Electrolysis of *E,E*-1,7-dibenzoyl-4-oxa-1,6-heptadiene (1b)

Electrolysis of 100 mg (0.0149 M) of **1b** with $Mg(ClO_4)_2$ electrolyte, at increasing voltages versus RE. The first 3.0 C at −2.0 V, then 1.8 C at −3.0 V, followed by 1.3 C at −3.5 V, and 6.0 C at −4.0 V. The reaction appeared complete after 12.1 C, or 38.4% (of the required charge) had passed through the cell. PTLC purification (1:4 ratio of EA/PET) of the 156 mg of recovered crude yielded *cis*-**2b** (26 mg, 39%), *trans*-**2b** (14 mg, 21%), and **3b** (19 mg, 28%), giving a total of 59 mg of pericyclic products (88%). While no other products were identified, 33 mg of starting material was recovered. The above percent of required charge is based upon the 100 mg of starting material being used up; this becomes 54.8% based upon the 67 mg of starting material used up (not recovered).

Electrolysis of 205 mg (0.0305 M) of **1b** with $LiClO_4$ electrolyte, at −1.3 V for 40.0 C (62.7% of required charge). PTLC separation of the 170 mg of crude yielded *cis*-**2b** (41 mg, 20%), *trans*-**2b** (42.2 mg, 21%), **3b** (4 mg, 2%), along with 2.8 mg of unreacted **1b**.

Electrolysis of 105 mg (0.0156 M) of **1b** with Bu_4NBF_4 electrolyte, at −1.6 V for 2.1 C and −2.0 V for 0.9 C. This corresponds to 9.4% of required charge. PTLC separation of the 108 mg of crude yielded *cis*-**2b** (12 mg, 11%), *trans*-**2b** (41 mg, 39%), **3b** (3 mg, 3%), and **4b** (11 mg, 11%).

Electrolysis of 28 mg (0.0042 M) of **1b** with Et_4NBF_4 electrolyte, and 157 mg (0.340 M) of benzil, at −1.4 V for 3.2 C. This corresponds to 36.2% of required charge, or a catalytic factor of 2.76. PTLC separation proved problematic due to the large benzil excess, however a yield of 19.1 mg (68%) of **4b** was obtained by NMR integration of several mixed **4b**/benzil PTLC bands. No other products or unreacted starting material were observed.

Electrolysis of 66 mg (0.0098 M) of *cis*-**2b** with $LiClO_4$ electrolyte, at −2.5 V for 27.5 C, −3.0 V for 4.5 C, and then at −3.5 V for a further 30.0 C. PTLC separation of the crude yielded *trans*-**2b** (17.3 mg, 32%), **3b** (4 mg, 7%), an

aldol product **6b** (5.7 mg, 11%), a dihydro product **7b** (11 mg, 20%), with a further 12 mg (18%) of unreacted *cis*-**2b**.

Electrolysis of 52 mg (0.0077 M) of *trans*-**2b** with $LiClO_4$ electrolyte, at −3.0 V for 11 C, −3.5 V for 130 C, and −4.0 V for 20 C. No product spots were observed until after ~40 C, indicating that no reaction was occurring, hence the continued flow of charge. PTLC of the 68 mg of crude yielded 8 mg of impure *trans*-**2b**, along with 19 mg of unidentified product (single benzoyl moiety). None of the characterized products (such as *cis*-**2b**) were observed.

4.5.1. Compound *cis*-2b.[6] ^{1}H NMR (500 MHz, $CDCl_3$): 3.42 (2H, m), 3.63 (2H, d.m, J=10.2 Hz), 4.14 (4H, m), 7.34 (4H, br.t, J=7.6 Hz), 7.45 (2H, br.t, J=7.3 Hz), 7.72 (4H, br.d, J=8.2 Hz); ^{13}C NMR (500 MHz in $CDCl_3$): 39.72, 47.70, 73.46, 127.81, 128.59, 132.8, 136.05, 198.08; NMR COSY (500 MHz), and X-ray crystallography confirm structure;[6] HRMS (CI+): calcd; 307.133420. Found; 307.132575.

4.5.2. Compound *trans*-2b.[6] ^{1}H NMR (500 MHz, $CDCl_3$): 3.36 (3H, br.m), 3.46 (1H, dd, J=4.6, 9.6 Hz), 3.68 (1H, d, J=9.8 Hz), 4.06 (1H, d, J=9.6 Hz), 4.41 (1H, m), 4.53 (1H, m), 7.45 (4H, m), 7.54 (2H, br.m), 7.90 (2H, m), and 8.01 (2H, m); ^{13}C NMR (500 MHz in $CDCl_3$): 39.71, 40.74, 42.99, 43.01, 69.27, 72.55, 128.29, 128.71, 128.76, 128.91, 133.41, 133.43, 135.27, 135.61, 196.70, 199.70; NMR COSY (500 MHz), and X-ray crystallography confirms the structure;[6] HRMS (CI+): calcd; 307.133420. Found; 307.133048.

4.5.3. Compound 3b.[6] ^{1}H NMR (500 MHz, $CDCl_3$): 2.99 (1H, m), 3.06 (1H, m), 3.58 (1H, m), 3.75 (1H, dd, J=4.4, 9.6 Hz), 4.17 (2H, m), 4.98 (1H, d, J=8.6 Hz), 5.58 (1H, d, J=4.2 Hz), 7.26 (2H, m), 7.48 (5H, m), 7.61 (1H, m), 8.08 (2H, m); ^{13}C NMR (500 MHz in $CDCl_3$): 35.54, 36.94, 70.30, 74.03, 76.30, 98.89, 124.65, 128.24, 128.44, 128.62, 129.51, 133.70, 134.44, 135.41, 151.80, 196.01; NMR COSY (500 MHz) and X-ray crystallography confirms the structure;[6] HRMS (CI+): calcd; 307.133420. Found; 307.132957.

4.5.4. Compound 4b. ^{1}H NMR (300 MHz, $CDCl_3$): 3.08 (1H, m), 3.17 (1H, d, J=5.7 Hz), 3.20 (1H, d, J=7.5 Hz), 3.85 (1H, m), 3.98 (1H, dd, J=3.3, 10.8 Hz), 4.23 (1H, dd, J=2.7, 10.8 Hz), 4.72 (1H, td, J<1.5, 6.0 Hz), 6.52 (1H, dd, J=1.8, 6.0 Hz), 7.48 (4H, br.t, J=7.5 Hz), 7.58 (2H, m), 8.00 (4H, m). X-ray crystallography confirms structure (CCDC 240331).

4.5.5. Compound 6b.[6] ^{1}H NMR (300 MHz, $CDCl_3$): 1.98 (1H, ddd, J=1.5, 8.1, 12.9 Hz), 2.45 (1H, dd, J=8.1, 12.9 Hz), 3.22 (2H, m), 3.64 (2H, dd, J=6.3, 9.0 Hz), 3.85 (2H, t, J=9.9 Hz), 4.12 (1H, d, J=9.6 Hz), 5.35 (1H, d, J=2.1 Hz), 7.14 (1H, m), 7.24 (2H, m), 7.40 (2H, m), 7.52 (2H, m), 7.59 (1H, m), 7.80 (2H, dd, J=1.5, 8.7 Hz).

4.5.6. Compound *cis*-7b. ^{1}H NMR (300 MHz, $CDCl_3$): 3.04 (4H, br.m), 3.16 (2H, dd, J=3.0, 14.1 Hz), 3.60 (2H, dd, J=4.2, 8.7 Hz), 4.12 (2H, m), 7.47 (4H, br.t, J=7.8 Hz), 7.58 (2H, br.t, J=7.8 Hz), 7.94 (4H, m); HRMS (CI+): calcd; 309.149070. Found; 309.149110.

4.6. Electrolysis of *E*,*E*-1,7-bis(4-chlorobenzoyl)-1,6-heptadiene (1c)

Electrolysis of 99 mg (0.012 M) of **1c** with Bu_4NBF_4 electrolyte, at −1.2 V for 2.1 C, −1.6 V for 2.2 C, and −1.8 V for 0.8 C. The reaction appeared complete after 5.0 C, or 19.5% (of required charge) had passed through the cell. PTLC purification of the 124 mg of recovered crude yielded *cis*-**2c** (11 mg, 11%), *trans*-**2c** (51.5 mg, 52%), and **3c** (11.5 mg, 12%), for a total yield of 74 mg of pericyclic products (75%). No starting material was recovered. However, a further 5 mg (5%) of **5c** was recovered.

Electrolysis of 55 mg (0.0067 M) of **1c** with 32 mg (0.0080 M) of benzophenone and Et_4NBF_4 electrolyte, at −1.8 V for 1.5 C (10.5% of required charge). **1c**/benzophenone=1:1.19. PTLC separation yielded *cis*-**2c** (6 mg, 11%), *trans*-**2c** (23 mg, 42%), and **3c** (4 mg, 7%), for a total yield of 33 mg of pericyclic products (60%). A further 7 mg (13%) of **5c** was recovered.

Electrolysis of 99 mg (0.012 M) of **1c** with 165 mg (0.036 M) of benzil and Et_4NBF_4 electrolyte, at −1.3 V for 2.5 C (9.7% of required charge). **1c**/benzil=1:1.2.96. PTLC separation yielded 28 mg (28%) of **5c** along with 42 mg (42%) of an unidentified polymer.

4.6.1. Compound *cis*-2c.[6] ^{1}H NMR (300 MHz, $CDCl_3$) 1.68 (2H, m), 1.82 (2H, dd, J=9.9, 2.4 Hz), 2.00 (2H, m), 3.16 (2H, m), 3.77 (2H, d, J=3.9 Hz), 7.32 (4H, d, J=8.4 Hz), 7.66 (4H, d, J=9.0 Hz); HRMS (CI+): calcd; 373.076210. Found 373.076164.

4.6.2. Compound *trans*-2c.[6] ^{1}H NMR (300 MHz, $CDCl_3$): 1.38 (2H, m), 1.58 (1H, m), 1.82 (3H, m), 3.04 (1H, dd, J=6.9, 13.2 Hz), 3.22 (1H, m), 4.20 (1H, dd, J=0.9, 7.5 Hz), 4.49 (1H, dd, J=2.4, 10.2 Hz), 7.44 (4H, dd, J=2.7, 8.4 Hz), 7.88 (2H, br. d, J=8.4 Hz), 7.95 (2H, br.d, J=9.0 Hz):); HRMS (CI+): calcd; 373.076210. Found; 373.075821.

4.6.3. Compound 3c.[6] ^{1}H NMR (300 MHz, $CDCl_3$): 1.41 (1H, m), 1.59 (2H, m), 1.78 (1H, m), 2.01 (2H, m), 2.68 (2H, m), 4.80 (1H, d, J=6.9 Hz), 5.52 (1H, d, J<1.5 Hz), 7.40 (2H, m), 7.47 (4H, m), 8.01 (2H, d, J=8.4 Hz); HRMS (CI+): calcd; 373.076210. Found; 373.076898.

4.6.4. Compound 5c. ^{1}H NMR (300 MHz, $CDCl_3$): 1.64 (1H, m), 1.72 (3H, m), 2.30 (2H, br.m), 2.79 (1H, dd, J=10.2, 14.7 Hz), 3.34 (1H, dd, J=3.6, 14.7 Hz), 3.43 (1H, br.s), 6.61 (1H, td, J=3.9, 1.2 Hz), 7.43 (3H, m), 7.51 (1H, m), 7.62 (2H, m), 7.99 (2H, m); HRMS (CI+): calcd; 373.076210. Found; 373.076307.

4.7. Electrolysis of *E*,*E*-1,7-bis(3,4-dichlorobenzoyl)-1,6-heptadiene (1d)

Electrolysis of 102 mg (0.0105 M) of **1d** with $LiClO_4$ and $Mg(ClO_4)_2$ electrolyte (both 0.10 M), at −4.0 V (first 1.5 C at −3.0 V). The reaction appeared complete after 17.0 C, or

76.3% (of required charge) had passed through the cell. PTLC purification of the 87 mg of recovered crude yielded *cis*-**2d** (34 mg, 33%), *trans*-**2d** (7 mg, 7%), and **3d** (16 mg, 16%), for a total yield of 57 mg of pericyclic products (56%). A further 6 mg (6%) of a product was isolated and identified as **6d**.

Electrolysis of 100 mg (0.0103 M) of **1d** with Et_4NBF_4 electrolyte, at −3.2 V for 3.0 C (first 0.75 C at −2.5 V, then 0.75 C at −3.0 V). This corresponds to 13.7% of required charge. PTLC purification of the 150 mg of crude yielded 3 mg (3%) of *trans*-**2d**, 17 mg (17%) of **5d**, and 35 mg (35%) of an unidentified polymer.

4.7.1. Compound *cis*-2d.[6] ^{1}H NMR (300 MHz, $CDCl_3$): 1.74 (2H, m), 1.85 (2H, dd, J=11.7, 3.3 Hz), 2.05 (2H, m), 3.19 (2H, d, J=2.4 Hz), 3.77 (2H, d, J=3.6 Hz), 7.46 (2H, d, J=8.4 Hz), 7.57 (2H, dd, J=8.7, 2.1 Hz), 7.81 (2H, d, J=2.1 Hz); HRMS (CI+): calcd; 440.998266. Found; 440.997859.

4.7.2. Compound *trans*-2d. ^{1}H NMR (300 MHz, $CDCl_3$): 1.38 (2H, m), 1.55 (1H, m), 1.83 (3H, m), 3.04 (1H, m), 3.24 (1H, m), 4.15 (1H, m), 4.47 (1H, dd, J=2.1, 10.2 Hz), 7.55 (1H, d, J=3.3 Hz), 7.57 (1H, d, J=3.0 Hz), 7.76 (1H, br.d), 7.81 (1H, br.d), 8.02 (1H, d, J=2.1 Hz) 8.08 (1H, d, J=1.8 Hz); HRMS (CI+): calcd; 440.998266. Found; 440.997697.

4.7.3. Compound 3d. ^{1}H NMR (300 MHz, $CDCl_3$): 1.60 (2H, m), 1.85 (2H, m), 2.07 (2H, m), 2.83 (2H, m), 5.09 (1H, d, J=6.9 Hz), 5.73 (1H, d, J<3 Hz), 7.39 (2H, m), 7.62 (3H, m), 7.74 (3H, m), 7.95 (4H, m), 8.15 (1H, m), 8.74 (1H, br.s); HRMS (CI+): calcd; 440.998266. Found; 440.997720.

4.7.4. Compound 5d. ^{1}H NMR (300 MHz, $CDCl_3$): 1.73 (4H, m), 2.31 (2H, br.m), 2.84 (1H, dd, J=9.6, 15.0 Hz), 3.66 (1H, dd, J=3.6, 15.0 Hz), 3.40 (1H, br.s), 6.66 (1H, t, J=3.3 Hz), 7.51 (2H, m), 7.56 (1H, d, J=8.4 Hz), 7.74 (1H, d, J=1.8 Hz), 7.90 (1H, dd, J=2.1, 8.4 Hz), 8.12 (1H, d, J=2.1 Hz); HRMS (CI+): calcd; 440.998266. Found; 440.998110.

4.7.5. Compound 6d. ^{1}H NMR (300 MHz, $CDCl_3$): 1.71 (3H, m), 1.98 (1H, m), 2.17 (1H, m), 2.34 (1H, m), 2.96 (3H, m), 3.17 (1H, br.d, J=17.4 Hz), 3.65 (1H, d, J=9.0 Hz), 5.24 (1H, d, J<1.5 Hz), 7.31 (1H, m), 7.54 (2H, m), 7.76 (1H, br.d), 7.81 (1H, d, J=2.1 Hz), 8.00 (1H, m); HRMS (CI+): calcd; 443.013916. Found; 443.012405.

4.8. Electrolysis of *E*,*E*-1,7-di-1-naphthoyl-1,6-heptadiene (1e)

Electrolysis of 97 mg (0.0109 M) of **1e** with Bu_4NBF_4 electrolyte, at −1.8 V (first 3.0 C at −1.5 V). The reaction appeared complete after 4.5 C, or 19.4% (of required charge) had passed through the cell. PTLC purification of the 123 mg of recovered crude yielded *cis*-**2e** (14 mg, 14%), *trans*-**2e** (28 mg, 29%), and **3e** (8 mg, 8%), for a total yield of 50 mg of pericyclic products (51%). No starting material was recovered. A further 16 mg (17%) of **5e** was recovered.

Electrolysis of 104 mg (0.0117 M) of **1e**, with Et_4NBF_4 electrolyte and 25 mg of acetic acid, giving a 1.6:1 excess of acetic acid. Initially at −2.5 V for 15.0 C and then at −3.0 V for 32.0 C. PTLC purification of the crude yielded *trans*-**2e** (6.0 mg, 6%), **5e** (2.8 mg, 3%), **6e** (14.1 mg, 14%), and **7e** (39.2 mg, 35%).

Electrolysis of 98 mg (0.0110 M) of **1e** with Bu_4NBF_4 electrolyte, at −1.5 V. The reaction was stopped after 3.4 C, or 14.5% (of required charge, corrected to 18.4%) had passed through the cell. PTLC purification of the 122 mg of recovered crude yielded *cis*-**2e** (16.6 mg, 21%), *trans*-**2e** (13 mg, 17%), and **3e** (8 mg, 10%), for a total yield of 37.6 mg of pericyclic products (48%). 20.4 mg (21%) of starting material was recovered, along with 5 mg (6%) of **5e**. Reaction is 79% complete based upon recovered **1e**.

4.8.1. Compound *cis*-2e.[6] ^{1}H NMR (300 MHz, $CDCl_3$) 1.74 (2H, m), 1.93 (2H, dd, J=14.1, 5.4 Hz), 2.15 (2H, m), 3.29 (2H, d, J=2.4 Hz), 4.08 (2H, d, J=4.2 Hz), 7.45 (4H, m), 7.74 (4H, m); 7.81 (4H, m), 8.22 (2H, s); HRMS (CI+): calcd; 405.185455. Found 405.185760.

4.8.2. Compound *trans*-2e.[6] ^{1}H NMR (300 MHz, $CDCl_3$): 1.45 (1H, m), 1.62 (1H, m), 1.85 (2H, m), 1.99 (2H, m), 3.16 (1H, m), 3.35 (1H, m), 4.50 (1H, m), 4.79 (1H, dd, J=2.4, 10.2 Hz), 7.58 (4H, m), 7.89 (4H, m), 8.03 (4H, br.m), 8.48 (1H, br.s), 8.60 (1H, br.s); HRMS (CI+): calcd; 405.185455. Found; 405.186095.

4.8.3. Compound 3e.[6] ^{1}H NMR (300 MHz, $CDCl_3$): 1.60 (2H, m), 1.85 (2H, m), 2.07 (2H, m), 2.83 (2H, m), 5.09 (1H, d, J=6.9 Hz), 5.73 (1H, d, J<3 Hz), 7.39 (2H, m), 7.62 (3H, m), 7.74 (3H, m), 7.95 (4H, m), 8.15 (1H, m), 8.74 (1H, br.s); HRMS (CI+): calcd; 405.185455. Found; 405.186005.

4.8.4. Compound 5e.[11] ^{1}H NMR (300 MHz, $CDCl_3$): 1.71 (1H, m), 1.87 (3H, m), 2.35 (2H, br.m), 3.00 (1H, dd, J=11.4, 15.6 Hz), 3.66 (1H, dd, J=3.6, 15.6 Hz), 3.77 (1H, br.s), 6.75 (1H, br.t), 7.60 (4H, m), 7.92 (5H, m), 7.99 (1H, m), 8.05 (1H, m), 8.14 (1H, m), 8.22 (1H, s), 8.71 (1H, s).

4.8.5. Compound 6e.[6] ^{1}H NMR (300 MHz, $CDCl_3$). Partial only: 1.60 (m), 1.91 (m), 3.20 (2H, m), 5.74 (1H, d, J=1.8 Hz), 7.41 (2H, m), 7.59 (6H, br.m), 7.76 (2H, m), 7.87 (2H, m), 8.00 (2H, m).

4.8.6. Compound *trans*-7e. ^{1}H NMR (300 MHz, $CDCl_3$): 1.35 (1H, m), 1.67 (2H, m), 1.88 (1H, m), 2.04 (2H, m), 2.31 (1H, m), 2.78 (1H, m), 2.95 (1H, dd, J=8.1, 15.6 Hz), 3.10 (1H, dd, J=8.1, 16.2 Hz), 3.27 (1H, dd, J=5.7, 15.3 Hz), 3.38 (1H, dd, J=4.8, 16.2 Hz), 7.56 (4H, m), 7.88 (4H, m), 7.95 (2H, br.d, J=7.8 Hz), 8.02 (2H, m), 8.47 (2H, br.d, J=6.0 Hz); HRMS (CI+): calcd; 407.201105. Found; 407.202010.

4.9. Electrolysis of *E*,*E*-1,7-bis(4-phenylbenzoyl)-1,6-heptadiene (1f)

Electrolysis of 76 mg (0.0076 M) of **1f** with Bu_4NBF_4 electrolyte (in a 1:1 THF/acetonitrile solution), at −3.5 V (first 1.8 C at −2.5 V, then 1.1 C at −3.0 V). The reaction

appeared complete after 11.7 C, or 69.6% (of required charge) had passed through the cell. PTLC purification of the 107 mg of recovered crude yielded *trans*-**2f** (9 mg, 12%). Also recovered was 13 mg (17%) of **5f**.

Electrolysis of 55 mg (0.0055 M) of **1f** with $Mg(ClO_4)_2$ (0.1 M in 1:1 THF/acetonitrile) at −2.0 V for 5.0 C (corrected for recovered **1f** to 53.7% of required charge), PTLC purification of the 61 mg of crude yielded *cis*-**2f** (9 mg, 21%), *trans*-**2f** (3.1 mg, 7%), and **3f** (11 mg, 25%), for a total yield of 23.1 mg of pericyclic products (53%). 11 mg of unreacted **1f** was recovered, allowing the corrected yields given above. Two additional products were isolated; 5.8 mg (13%) of **6f**; and 3.2 mg (7%) of **7f**.

4.9.1. Compound *cis*-2f.[6] ^{1}H NMR (300 MHz, $CDCl_3$): 1.84 (4H, m), 2.06 (2H, m), 3.27 (2H, m), 3.92 (2H, m), 7.37 (6H, m), 7.55 (8H, m), 7.84 (4H, d, J=8.7 Hz).

4.9.2. Compound *trans*-2f. ^{1}H NMR (300 MHz, $CDCl_3$): 1.47 (2H, m), 1.66 (2H, m), 1.91 (2H, m), 3.13 (1H, m), 3.30 (1H, m), 4.33 (1H, m), 4.61 (1H, m), 7.45 (6H, m), 7.65 (2H, m), 7.70 (2H, d, J=8.4 Hz), 8.04 (2H, d, J=9.0 Hz), 8.11 (2H, d, J=8.7 Hz); HRMS (CI+): calcd; 457.216755. Found; 457.215380.

4.9.3. Compound 3f. ^{1}H NMR (300 MHz, $CDCl_3$): 1.56 (3H, m), 1.78 (1H, m), 2.05 (2H, m), 2.75 (2H, m), 4.93 (1H, m), 5.61 (1H, m), 7.40–7.72 (12H, m), 8.19 (2H, m): calcd; 457.216755. Found; 457.218026.

4.9.4. Compound 5f. ^{1}H NMR (300 MHz, $CDCl_3$): 1.67 (1H, m), 1.78 (3H, m), 2.31 (2H, br.m), 2.85 (1H, dd, J=10.5, 14.7 Hz), 3.47 (1H, dd, J=6.6, 13.8 Hz), 3.54 (1H, br.s), 6.70 (1H, m), 7.43 (6H, m), 7.66 (6H, m), 7.79 (2H, d, J=8.4 Hz), 8.03 (2H, d, J=8.7 Hz), 8.16 (2H, d, J=8.7 Hz); HRMS (CI+): calcd; 457.216755. Found; 457.216312.

4.9.5. Compound 6f.[6] ^{1}H NMR (300 MHz, $CDCl_3$). Partial only: 3.94 (1H, d, J=8.7 Hz), 5.63 (1H, d, $J\sim$1.5 Hz).

4.9.6. Compound *cis*-7f. ^{1}H NMR (300 MHz, $CDCl_3$): 1.34 (2H, m), 1.67 (2H, m), 2.02 (2H, m), 2.24 (2H, m), 2.98 (2H, dd, J=7.2, 17.4 Hz), 3.26 (2H, dd, J=4.5, 16.2 Hz), 7.44 (6H, m), 7.65 (8H, m), 8.03 (4H, d, J=8.7 Hz); HRMS (CI+): calcd; 459.232406. Found; 459.231734.

4.10. Electrolysis of *E*,*E*-1-acetyl-7-benzoyl-1,6-heptadiene (1g)

Electrolysis of 98 mg (0.018 M) of **1g** with $Mg(ClO_4)_2$ electrolyte, at −4.5 V for 150 C (initial 4.0 C at −4.0 V, last 16 C at −5.0 V), corresponding to 459% of required charge. PTLC separation yielded *cis*-**2g** (7 mg, 9%), and **7g** (14 mg, 17%), along with 11 mg (13%) of an unidentified product, tentatively described as an isomer of **7g** (LRMS (CI+): 245, 227). 16 mg of unreacted **1g** was also recovered.

Electrolysis of 73 mg (0.014 M) of **1g** with Et_4NBF_4 electrolyte, at −2.0 V for 16.0 C (initial 2.2 C at −1.6 V), corresponding to 55.0% of required charge. PTLC separation yielded two isomers of *trans*-**2g**, 9 mg (12%) of the isomer where the benzoyl group is *syn* to the cyclopentane ring, and 5 mg (7%) with an *anti* benzoyl group.

4.10.1. Compound *cis*-2g.[6] ^{1}H NMR (300 MHz, $CDCl_3$): 1.59 (2H, m), 1.68 (4H, br.m), 2.03 (3H, s), 3.00 (2H, m), 3.11 (1H, m), 3.79 (1H, dd, J=4.5, 9.9 Hz), 7.45 (2H, br.t, J=7.2 Hz), 7.52 (1H, br.t, J=7.2 Hz), 7.83 (2H, br.d, J=8.1 Hz); HRMS (CI+): calcd; 243.138505. Found; 243.138743.

4.10.2. Compound *trans*-2g (benzoyl group *syn* to the cyclopentane ring). ^{1}H NMR (300 MHz, $CDCl_3$): 1.36 (2H, m), 1.74 (4H, m), 2.13 (3H, s), 2.93 (1H, m), 3.13 (1H, m), 3.49 (1H, t, J=8.1 Hz), 4.32 (1H, dd, J=2.1, 10.5 Hz), 7.47 (2H, br.t, J=7.2 Hz), 7.57 (1H, br.t, J=6.9 Hz), 7.93 (1H, br.d, J=7.2 Hz). X-ray crystallography confirms structure (CCDC240332).

4.10.3. Compound *trans*-2g.[6] **(benzoyl group *anti* to the cyclopentane ring)** ^{1}H NMR (300 MHz, $CDCl_3$): 1.58 (2H, m), 1.80 (4H, m), 2.11 (3H, s), 2.94 (1H, m), 3.07 (1H, m), 3.38 (1H, m), 3.86 (1H, dd, J=2.4, 10.5 Hz), 3.99 (1H, t, J=6.3 Hz), 7.45 (2H, br.t, J=7.2 Hz), 7.55 (1H, br.t, J=7.2 Hz), 7.95 (1H, br.d, J=7.2 Hz).

4.10.4. Compound 7g. ^{1}H NMR (300 MHz, $CDCl_3$). 1.23 (2H, m), 1.61 (2H, m), 1.98 (4H, br.m), 2.13 (3H, s), 2.40 (1H, dd, J=7.8, 16.8 Hz), 2.67 (1H, dd, J=4.2, 16.8 Hz), 2.91 (1H, dd, J=7.8, 16.5 Hz), 3.14 (1H, dd, J=4.2, 16.8 Hz), 7.46 (2H, br.t, J=7.5 Hz), 7.56 (1H, br.t, J=7.2 Hz), 7.95 (1H, br.d, J=7.2 Hz); HRMS (CI+): calcd; 245.154155. Found; 245.154390.

4.11. Electrolysis of *E*,*E*-1,7-diacetyl-1,6-heptadiene (1h)

Electrolysis of 97 mg (0.025 M) of **1h** with Et_4NBF_4 electrolyte, at −2.5 V for 10.0 C (initial 4.0 C at −2.0 V). ^{1}H NMR (300 MHz, $CDCl_3$) of the 121 mg of recovered crude showed only starting material present (plus electrolyte).

4.12. Electrolysis of *E*,*E*-7-ethoxy-1-benzoyl-1,6-heptadiene (1i)

Electrolysis of 117 mg (0.020 M) of **1i** with $LiClO_4$ electrolyte (0.3 M), at −2.0 V for 10.0 C, −2.2 V for 20.0 C, and −3.0 V for 10.0 C (136% of required charge). PTLC separation yielded 23 mg (28%) of one isomer of *trans*-**2i**. Thought to be the same isomer as the major isomer seen in the **1g** electrolysis (based upon NMR comparison). A further 3 mg (4%) of the alternate *trans*-**2i** isomer was also obtained. 34 mg of starting material **1i** was recovered.

Electrolysis of 136 mg (0.023 M) of **1i** with Et_4NBF_4 electrolyte, at −2.0 V for 10.5 C. Yielding only unidentified polymers

4.12.1. Compound *trans*-2i (benzoyl group *syn* to the cyclopentane ring). ^{1}H NMR (300 MHz, $CDCl_3$): 0.98 (3H, t, J=7.2 Hz), 1.63 (2H, m), 1.72 (2H, m), 1.91 (2H, m), 3.04 (2H, m), 3.22 (1H, m), 3.69 (1H, dd, J=5.1, 9.9 Hz), 3.87

(2H, q, $J=7.2$ Hz), 7.43 (2H, br.t, $J=8.1$ Hz), 7.53 (1H, br.t, $J=6.9$ Hz), 7.84 (1H, br.d, $J=7.2$ Hz). HRMS (CI+): calcd; 273.149070. Found; 273.148638.

4.12.2. Compound *trans*-2i (benzoyl group *anti* to the cyclopentane ring). ^{1}H NMR (300 MHz, $CDCl_3$): 0.98 (3H, t, $J=7.2$ Hz), 1.69 (4H, m), 2.01 (2H, m), 2.99 (1H, m), 3.21 (1H, m), 3.38 (1H, m), 4.14 (2H, q, $J=7.2$ Hz), 4.34 (1H, dd, $J=2.7$, 10.5 Hz), 7.47 (2H, br.t, $J=6.3$ Hz), 7.56 (1H, br.t, $J=6.9$ Hz), 7.93 (1H, br.d, $J=6.6$ Hz). HRMS (CI+): calcd; 273.149070. Found; 273.148198.

4.13. Electrolysis of *E,E*-1,7-dicarbethoxy-1,6-heptadiene (1j)

Electrolysis of 112 mg (0.021 M) of **1j** with Et_4NBF_4 electrolyte, at −2.5 V for 10.0 C, corresponding to 22.2% of required charge. PTLC purification of the 112 mg of recovered crude yielded 47 mg (42%) of **5j**. No starting material was recovered.

Electrolysis of 96 mg (0.018 M) of **1j** with $LiClO_4$ electrolyte, at −3.5 V for 4.5 C, −3.5 V for 7.9 C, and −4.0 V for 55 C. ^{1}H NMR (300 MHz, $CDCl_3$) of the recovered crude showed only starting material present.

4.13.1. Compound 5j. ^{1}H NMR (500 MHz, $CDCl_3$): 1.26 (3H, t, $J=7.5$ Hz), 1.29 (3H, t, $J=7.0$ Hz), 1.64 (4H, m), 2.18 (2H, br.m), 2.27 (1H, dd, $J=10.5$, 15.0 Hz), 2.64 (1H, dd, $J=3.5$, 15.0 Hz), 3.09 (1H, br.s), 4.16 (4H, m), 7.03 (1H, t, $J=4.0$ Hz). ^{13}C NMR (500 MHz in $CDCl_3$): 14.21 (2C), 17.11, 25.77, 26.52, 29.92, 38.40, 60.20, 60.26, 132.79, 140.99, 166.86, 172.53; NMR COSY (500 MHz) (consistent with structure). HRMS (CI+): calcd; 241.143984. Found; 241.142945.

4.14. X-ray data

Crystallographic data (excluding structure factors) for **4b** and the primary *trans*-**2g** isomer, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 240331 and CCDC 240332, respectively. Copies of the data can be obtained, free of charge, via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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