

Interconversion and rearrangement of radical cations. Part 2.¹ Photoinduced electron transfer and electrochemical oxidation of 1,4-bis(methylene)cyclohexane



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The photoinduced electron transfer and electrochemical oxidation of 1,4-bis(methylene)cyclohexane (**2**) in acetonitrile have been studied in the presence and absence of a nucleophile (methanol). The photoinduced electron transfer reactions of **2** in acetonitrile–methanol solution with 1,4-dicyanobenzene (**8**) as the electron acceptor gives two products: 4-(methoxymethyl)-1-methylenecyclohexane (**16**) and 4-(4-cyanophenyl)-4-(methoxymethyl)-1-methylenecyclohexane (**17**). These products arise from nucleophilic attack on the radical cation followed by either reduction and protonation or combination with the radical anion of the electron acceptor, 1,4-dicyanobenzene (**8**^{•-}). These results are in accord with the proposed mechanism of the photochemical nucleophile–olefin combination, aromatic substitution (photo-NOCAS) reaction. In the absence of a nucleophile, the photoinduced electron transfer reaction of **2** gives rise to several interesting and unexpected products **18–25** which result from complex reaction mechanisms involving radical, ionic and radical ion intermediates.

The electrooxidation of **2** in acetonitrile in the presence of methanol leads to products **27–35**. Under these conditions the radical cation **2**^{•+} reacts with the nucleophile followed by a second oxidation and subsequent reactions leading to products (electrochemical–chemical–electrochemical, ECE). One of the products (**28**) is the result of protonation of **2** followed by nucleophilic attack. The electrochemical oxidation of **2** in acetonitrile (no methanol) yields **2**^{•+} which is deprotonated and then further oxidized to give **39–43**. These products arise from ionic intermediates (ECE); oxidation of **2** all the way to aromatic compounds was observed in **39–41**.

In none of these experiments was there any evidence for the formation of cyclized products, nor was there any indication of carbon–carbon bond cleavage in **2**^{•+}. The products are consistent with the initial formation of the intermediate radical cation. The products as well as the possible mechanisms of formation of these species are discussed.

Introduction

Radical cations are important intermediates in many chemical and biological reactions. They are commonly formed using techniques such as photoinduced electron transfer,² electrochemical oxidation,³ mass spectrometry⁴ and radiolytic oxidation.⁵ Upon formation, many reactions can take place, both unimolecular (*e.g.* bond cleavage, cyclization, isomerization, rearrangement) and bimolecular (*e.g.* dimerization, nucleophilic addition, deprotonation).

In a previous paper we reported on the possible interconversions and rearrangements of some C₄H₆^{•+} and C₈H₁₂^{•+} radical cations: methylenecyclopropane (**1**^{•+}), 1,4-bis(methylene)cyclohexane (**2**^{•+}), tricyclo[2.2.2.0^{1,4}]octane (**3**^{•+}), dispiro[2.0.2.2]octane (**4**^{•+}) and dispiro[2.1.2.1]octane (**5**^{•+}) (Fig. 1).¹

The long term objective of this study is to understand the mechanisms for the interconversion and rearrangement of these C₈H₁₂^{•+} radical cations. The first part of this series¹ described the application of *ab initio* molecular orbital theory to predict the rearrangement and interconversion of these five isomeric species. Some of these reaction pathways are briefly indicated in Scheme 1 (relative energies of the species given in kcal mol⁻¹).[†]

The most stable of these structures is the 1,4-bis(methylene)cyclohexane radical cation (**2**^{•+}). Note, however, that the [2.2.2]propellane radical cation (**3**^{•+}) is only 5 kcal mol⁻¹ higher in energy. Also, several of these radical cations are expected to undergo spontaneous rearrangements and/or bond cleavage.

The most exothermic reactions are those combining **1** with its radical cation (**1**^{•+}) or with trimethylenemethane radical cation

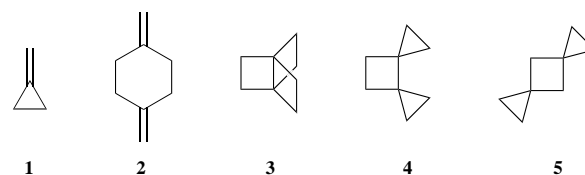


Fig. 1 Compounds of interest studied by *ab initio* methods as described in ref. 1 (see text)

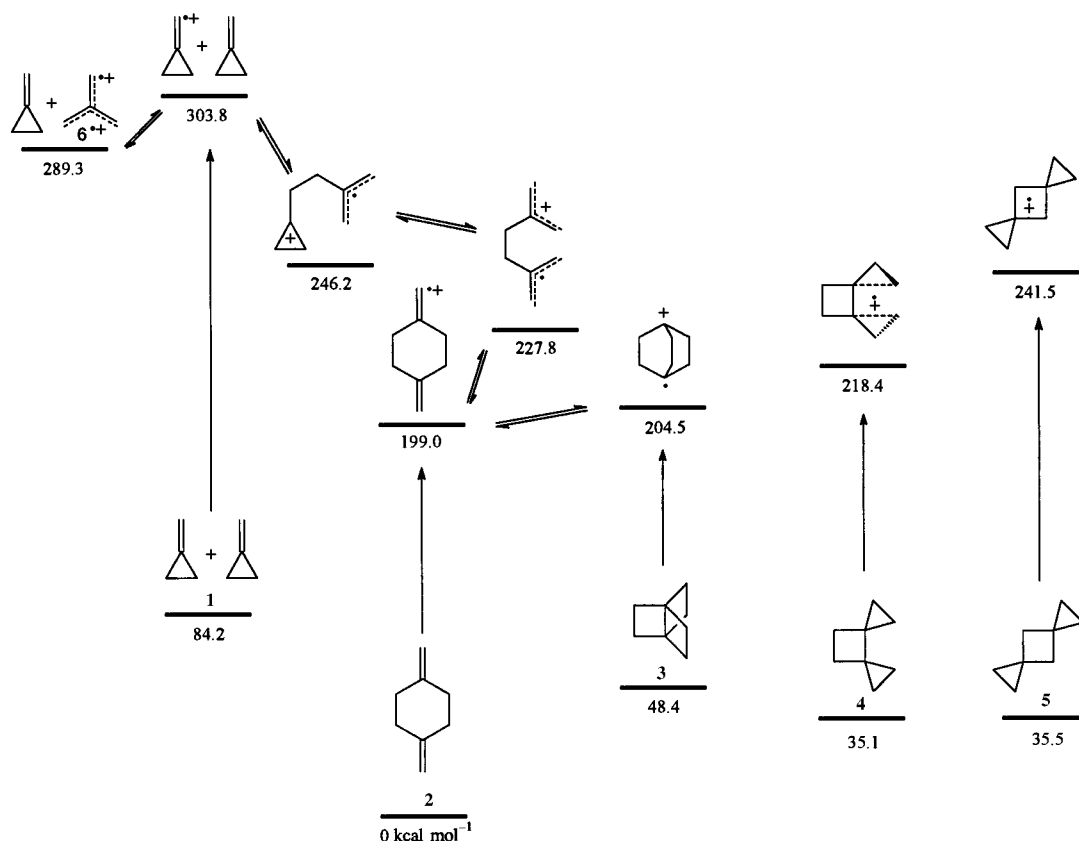
(**6**^{•+}). The calculations, relevant to the gas phase, identified only one type of dimeric radical cation.

Relevant experimental work has been limited and there are no reports involving the reactivity of these radical cations. Most of the work has focussed on [2.2.2]propellane (**3**).⁶ The parent molecule has never been isolated but the synthesis of a substituted propellane was reported.^{6a} In one of the attempts to synthesize **3**, **2** was used as the starting material.^{6c} However, the 1,4-diradical (**7**) is also a minimum on the potential energy surface,⁷ and the barrier between **3** and **7** is small which leads to a rapid cleavage back to **2** (Scheme 2).^{7c}

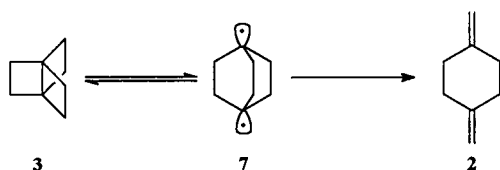
Reaction of triplet **1** (**1**¹) with **1**^{•+} results in the formation of **2** since **1**¹ has no other favourable decay mechanism.⁸ Thermal dimerization of **1** results in the formation of **4**,^{9b,c} whereas **5** can be formed by the metal-catalysed dimerization.^{9a,d-f}

In this project (Part 2) we have characterized the reactivity of the most stable isomer, the radical cation of 1,4-bis(methylene)cyclohexane (**2**^{•+}), under four distinct reaction conditions. The major products from the electrochemical anodic oxidation in acetonitrile solution with and without added nucleophile (methanol) have been identified, as well as the major products

[†] 1 cal = 4.184 J.



Scheme 1



Scheme 2

resulting from the photochemical electron transfer to the singlet excited state of 1,4-dicyanobenzene (**8**) in the presence and absence of a nucleophile (methanol). Several interesting (unexpected) products were formed and the possible mechanisms for the formation of these products are discussed.

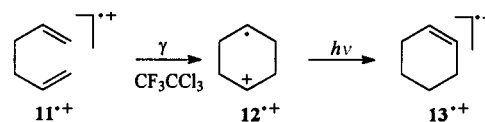
While these results are interesting in their own right, this work also provides the foundation for the next phase of the continuing study, that is, subjecting the higher energy species to these same reaction conditions.

Results and discussion

Photoinduced electron transfer of 1,4-bis(methylene)cyclohexane (**2**) in the presence of a nucleophile

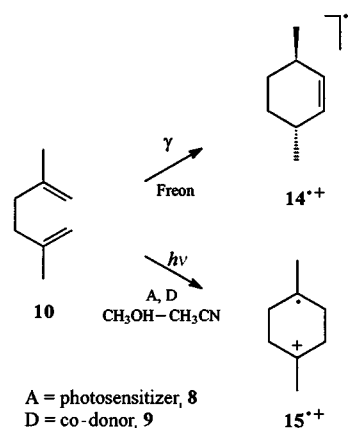
In the presence of a nucleophile radical cations usually undergo rapid nucleophilic addition.^{10,11} Under standard conditions for the photochemical nucleophile-olefin combination, aromatic substitution (photo-NOCAS) reaction, methanol is present and acts as the nucleophile; the 1:1:1 adduct (olefin-nucleophile-aromatic) is usually the major product.¹⁰ In the absence of a nucleophile other processes take place.^{12,13a} For example, when a radical cation is oriented properly, cyclization can occur,¹³ usually in competition with other reactions. Cyclized products are observed in the photo-NOCAS reaction of 2,5-dimethylhexa-1,5-diene (**10**),^{13a} 2,6-dimethylhepta-1,6-diene,^{13b} 6-methylhept-5-en-2-ol and 5-methylhex-5-en-2-ol^{13c} and (*R*)-(+)- α -terpineol.^{13d} Note that hexa-1,5-diene (**11**) does not give cyclized products upon irradiation in the presence of 1,4-dicyanobenzene (**8**, electron acceptor) and biphenyl (**9**,

co-donor) in acetonitrile or in acetonitrile-methanol mixtures.^{13a} However, in the radiolytic oxidation of **11** in a CF_3CCl_3 matrix the cyclized radical cation (**12**^{•+}) was observed.¹⁴ This species then rearranged to give the cyclohexene radical cation (**13**^{•+}) upon photobleaching or annealing of the matrix (Scheme 3).



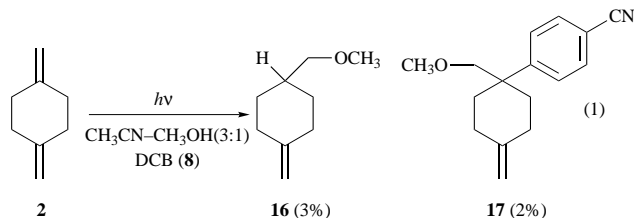
Scheme 3

Under similar radiolytic conditions the cyclized product from 2,5-dimethylhexa-1,5-diene radical cation (**10**^{•+}), *trans*-3,6-dimethylcyclohexene radical cation (**14**^{•+}), was observed.¹⁵ However, the products from the photo-NOCAS reaction of **10** clearly indicate that **10**^{•+} cyclizes to **15**^{•+} (Scheme 4).^{13a} No rearrangement was observed under these conditions.



Scheme 4

1,4-Bis(methylene)cyclohexane (**2**) reacts under photo-NOCAS conditions to give two products in low yields [reaction (1)]: the 1:1 (alkene-methanol) adduct 4-(methoxymethyl)-1-



methylenecyclohexane (**16**) and the 1:1:1 (alkene-methanol-aromatic) adduct 4-(4-cyanophenyl)-4-(methoxymethyl)-1-methylenecyclohexane (**17**). The yields of the products are based on the amount of **2** initially present in the mixture. The progress of the reaction was followed by capillary column gas chromatography with either a flame ionization detector (GC-FID) or mass spectrometry (GC-MS). The ratio of the products did not change during the irradiation. Both products arise from methanol attack on the terminal end of the methylene group of the initially formed radical cation ($2^{+\cdot}$) to form the (methoxymethyl)methylenecyclohexyl radical. The 1:1 (alkene-methanol) adduct, 4-(methoxymethyl)-1-methylenecyclohexane (**16**), results from reduction of this β -methoxy radical to the anion by $8^{\cdot-}$, followed by protonation. This mechanism was confirmed by performing the same experiment in acetonitrile-methanol- $[^2\text{H}]_2\text{O}$. The mass spectrum of **16** obtained from this experiment showed a molecular ion at m/z 141. Reduction of the β -methoxy radical to the anion, followed by deuteration (by methanol- $[^2\text{H}]_2\text{O}$) can account for this molecular ion ($\text{C}_9\text{H}_{15}\text{DO}$).

The (1:1:1) photo-NOCAS adduct, 4-(4-cyanophenyl)-4-(methoxymethyl)-1-methylenecyclohexane (**17**), is a result of a coupling of the β -methoxy radical with $8^{\cdot-}$, and subsequent loss of cyanide anion. These results are in good agreement with the mechanism proposed for the photo-NOCAS reaction.^{10,13} Adduct **17** can be described as the *anti*-Markovnikov product.^{10b} Attempts to detect the other regioisomer, the Markovnikov product, using GC-MS in the selected ion monitoring (SIM) mode showed that only one product with molecular weight 241 was formed. The photo-NOCAS reaction of the structurally related compound, isobutylene (2-methylpropene), gave two 1:1:1 adducts in a 26:1 ratio;^{10f,g} the major product was the *anti*-Markovnikov regioisomer. The total yield in this reaction was 54%. Since the yields in reaction (1) are low, it is possible that the Markovnikov regioisomer was formed below the detection limit. The spin and charge densities in $2^{+\cdot}$, calculated at the MP2/6-31G**//HF/6-31G* level of theory,¹ are almost equally distributed over both carbons of one of the methylene groups; solely based on this fact, one would expect some attack of the nucleophile on the tertiary carbon. This, however, would lead to a primary radical in contrast to attack on the terminal carbon which results in the formation of a tertiary radical. Obviously, radical stability is important.¹⁶

The low yields and efficiency of this reaction are understandable in view of the relatively high oxidation potential of **2** (2.49 V vs. SCE; Table 1) which influences the rate of electron transfer. The initial electron transfer will occur at the diffusion-controlled limit when the ΔG_{et} for the process is exergonic by more than 5 kcal mol⁻¹.¹⁷ The ΔG_{et} can be calculated using the Weller equation [eqn. (2)].¹⁷ The oxidation potentials and

$$\Delta G_{\text{et}} = F[E_2^{\text{ox}}(\text{D}) - E_2^{\text{red}}(\text{A}) - e|\epsilon a|] - E_{0,0}(\text{A}) \quad (2)$$

calculated ΔG_{et} values for several compounds are given in Table 1. For **2** the rate of electron transfer will be close to the diffusion controlled limit.

Adding biphenyl (**9**) to the reaction mixture is known to increase both the yield and the efficiency of the photo-NOCAS

Table 1 Oxidation potentials of selected compounds and the calculated free energy change (ΔG_{et}) for the electron transfer process involving the singlet excited state of 1,4-dicyanobenzene (**8**) as the electron acceptor and the alkene or diene as the electron donor

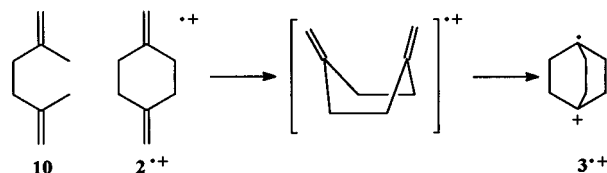
Compound	$E_2^{\text{ox}}/\text{V}^a$	$\Delta G_{\text{et}}/\text{kcal mol}^{-1b}$
2,5-Dimethylhexa-1,5-diene (10)	2.60 ^c	-0.7
1,4-Bis(methylene)cyclohexane (2)	2.49 ^d	-3.2
2-Methylpropene	2.99 ^e	+8.3

^a See Experimental section for details. ^b Based upon the Weller equation:¹⁷ $E_{0,0}$ (**8**) 97.6 kcal mol⁻¹, E_2^{red} (**8**) -1.66 V, the Coulombic attraction term was taken to be 1.3 kcal mol⁻¹.^{10f,c} Ref. 13a. ^d This work. ^e Ref. 10g.

Table 2 Influence of the methanol concentration on the product ratio **16**:**17**

[CH ₃ OH] ^a /mol l ⁻¹	Ratio 16 : 17
6.0	1.0
3.6	1.0
1.2	0.8
0.5	0.8
0.25	0.5
0.1	0.3

^a Concentration of **9** in these experiments was 0.05 mol l⁻¹.



Scheme 5

reaction.^{10,13} In the photo-NOCAS reaction of **2** the yields of **16** and **17** approximately doubled with a shorter irradiation time when **9** was used as the co-donor. The role of **9** is not yet fully understood. The explanation that is frequently used is that separation of the radical ion pair becomes more efficient since back electron transfer (BET) between $9^{+\cdot}$ and $8^{\cdot-}$ is slower because of the smaller reorganization energy for $9^{+\cdot}$ going back to **9**. Reducing the BET prolongs the lifetime of the radical cation and this may lead to other (side) reactions such as cyclization. For example, when 2,5-dimethylhexa-1,5-diene (**10**) was irradiated in the presence of **8** and **9**, both acyclic and cyclic products were observed, whereas without the co-donor **9** only acyclic products were formed.^{13a} The ratio of cyclic to acyclic products increased with increasing biphenyl concentration. This ratio also increased with decreasing methanol concentration. The mode of cyclization was shown to be 1,6-*endo,endo*. Cyclization of **2**, which obviously has some structural similarities to **10**, could therefore give $3^{+\cdot}$ (Scheme 5).

Calculations have shown that $3^{+\cdot}$ is only 5 kcal mol⁻¹ higher in energy than $2^{+\cdot}$.¹ However, note that cyclization of $2^{+\cdot}$ would require a boat-like transition state which would further increase the reaction barrier by *ca.* 7 kcal mol⁻¹.¹⁸ Experiments with **2** where the methanol concentration was lowered (0.1–6 M) and where the biphenyl concentration was increased (0.05–0.2 M) did not result in the formation of cyclized products. In all of these experiments only **16** and **17** were formed. The ratio of these products was dependent on the conditions used (Tables 2 and 3). Lowering the methanol concentration leads to increased amounts of the 1:1:1 adduct (**16**:**17** = 0.3–1.0). The same result is obtained when the biphenyl concentration is increased (**16**:**17** = 0.6–1.0).

Small amounts of other products were detected and, based on the GC-MS data, these compounds are believed to be 1:1 (alkene-aromatic) adducts. When the biphenyl (**9**) concentration was increased, products arising from **9** were also observed.

Table 3 Influence of the biphenyl (**9**) concentration on the product ratio **16**:**17**

[9] ^a /mol l ⁻¹	Ratio 16 : 17
0.2	0.6
0.1	1.1
0.05	1.0

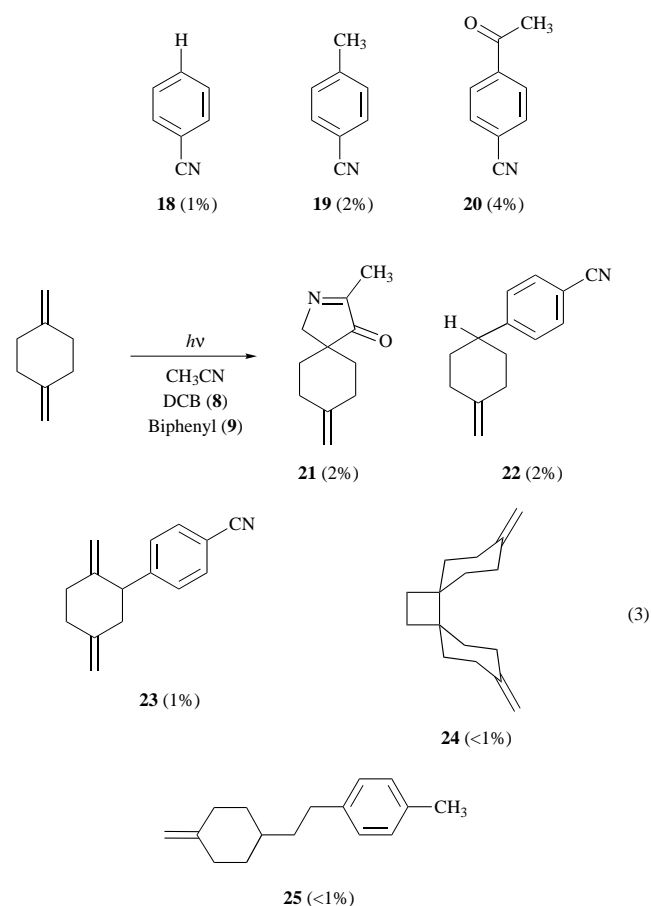
^a Methanol concentration in these experiments was 6.0 mol l⁻¹.

The products 2-cyanobiphenyl, 4-cyanobiphenyl and 3,5-dimethoxy-4-phenylcyclohexanecarbonitrile have been observed before.^{13a}

Photoinduced electron transfer of 1,4-bis(methylene)cyclohexane (**2**) in the absence of a nucleophile

Generation of an alkene radical cation in the absence of a nucleophile could lead to a number of reactions, e.g. cyclization or another type of rearrangement, as it would increase the lifetime of the radical cation. Other products that are often observed in these reactions are 1:1 (alkene–aromatic) adducts and dimers.

In the absence of a nucleophile, the photoinduced electron transfer reaction of **2** leads to a variety of interesting and, in some cases, unexpected products [reaction (3)].

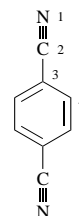


Of the two expected 1:1 adducts (**23** and **26**) only one [2-(4-cyanophenyl)-1,4-bis(methylene)cyclohexane (**23**)] was formed. In the early stages of the irradiation, GC–MS analysis of the photolysate indicates that both 1:1 adducts were present. After prolonged irradiation only **23** remained. Compound **26** has a lower oxidation potential than **23** because of the internal double bond and will therefore be more reactive towards further oxidation than **23**. There is some evidence that this secondary reaction takes place. One of the products found in the reaction mixture is 4-cyanotoluene (**19**) which is likely to be the result of the *p*-cyanobenzyl radical (**19'**). A hydrogen atom

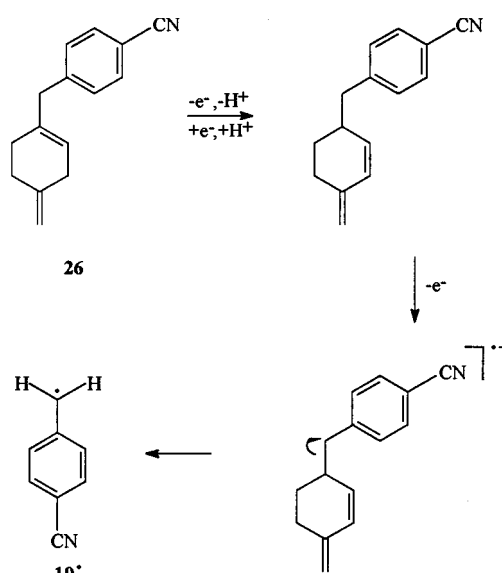
Table 4 Calculated (STO-3G) spin and charge densities for the radical anion of 1,4-dicyanobenzene (**8**^{•-})

Atom ^a	Spin density ^b	Charge density ^b
1	+0.849	-0.296
2	-0.792	+0.022
3	+0.536	-0.084
4	-0.047	-0.071

^a See Fig. 2 for numbering of atoms. ^b Hydrogens summed with heavy atoms.

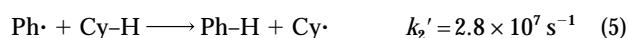
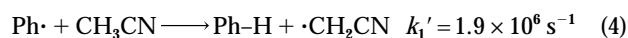
**Fig. 2** Atom numbering for the radical anion of 1,4-dicyanobenzene (**8**^{•-}). See Table 4 for the calculated (STO-3G) spin and charge densities.

abstraction from the solvent (or **2**) would then give **19**. To verify this, the reaction was also carried out in CD_3CN . The mass spectrum of **19** indicates deuterium incorporation, consistent with **19'** as an intermediate in the reaction. Also, analysis of the product mixture by GC–MS indicated the presence of a small amount of a product with a mass of 232. Based on the mass spectrum of this compound we conclude that this is the coupling product of two *p*-cyanobenzyl radicals. The benzylic radical (**19'**) is thought to arise by deprotonation of **26**^{•+} (a result of electron transfer from **26** to **8**^{•-}) leading to a conjugated diene which could then be further oxidized and undergo bond cleavage to give the *p*-cyanobenzyl radical (**19'**) (Scheme 6).

**Scheme 6**

The formation of benzonitrile (**18**) and 4-cyanoacetophenone (**20**) could be explained on the basis of both radical and ionic mechanisms, however, careful analysis of the possible mechanisms rules out the ionic mechanism. The observed products **18** and **20** could be formed by reaction of protonated acetonitrile with **8** or **8**^{•-}. However, the calculated^{10j} charge densities in **8**^{•-} show that the negative charge is mainly on the nitrogens and not on the *ipso* carbon (Fig. 2; Table 4) and reaction between these two species would therefore not lead to the observed products. Reaction of protonated acetonitrile with **8** is also unlikely since the *ipso* carbons in **8** are not likely to have a large negative charge density.

A radical mechanism is likely to involve the *p*-cyanophenyl radical which could be formed by loss of cyanide anion from **8**^{•-}. Hydrogen atom abstraction would lead to **18**, whereas addition to acetonitrile and further reaction (hydrolysis) would give **20**. The rate constants for the reaction of phenyl radical¹⁹ with acetonitrile ($k_1 = 1.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) and with cyclohexene (Cy-H: a model for **2**, $k_2 = 2.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) have been measured by laser flash photolysis.²⁰ These rate constants are most likely those of the hydrogen atom abstraction processes. Using the rate constants and the concentrations of the two species we can calculate the pseudo-first-order rate constants of the two competing processes in reactions (4) and (5).



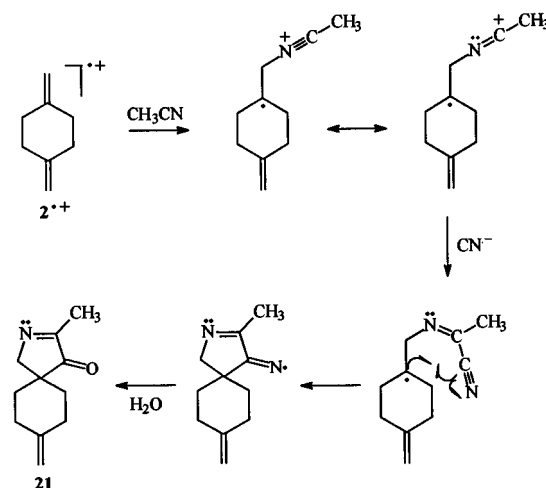
It is clear that hydrogen atom abstraction from **2** is favoured over that from acetonitrile despite the large difference in concentration between these two hydrogen atom donors. Since hydrogen atom abstraction from acetonitrile by *p*-cyanophenyl radical is a very slow process, the addition pathway might become more favourable. There are many examples of intramolecular radical addition reactions to nitriles.²¹ For example, Ogibin *et al.*^{21b} found that upon generation of the 4-cyanobutyl radical in an aqueous medium, cyclopentanone was the major product. Intermolecular radical additions to nitriles are not very well known. In fact, Ingold and co-workers^{21c} found that the phenyl radical (and others) did not add to pivalonitrile. On the other hand, Shelton and Uzelmeier^{21d} found that both phenyl and cyclohexyl radicals added to benzonitrile. Addition of radicals to acetonitrile is rarely observed,²² however, more evidence for this pathway was obtained by refluxing a solution of dibenzyl peroxide in acetonitrile. Analysis (GC-FID and GC-MS) of samples taken from the reaction mixture showed that even under these conditions a trace amount of acetophenone was formed.

The observed product ratio **18**:**20** is 1:4. This ratio was obtained after prolonged irradiation (41 days). After shorter irradiation times this ratio varied from *ca.* 1:1 to 1:2. This indicates that addition of acetonitrile to the *p*-cyanophenyl radical is competitive with the hydrogen atom abstraction process. If the measured value for the reaction of phenyl radical with acetonitrile is the rate constant for hydrogen atom abstraction ($k_1 = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$)¹⁹ and if we assume that addition of the *p*-cyanophenyl radical to acetonitrile is the rate-determining step in the formation of **20** we can calculate a minimum rate constant of *ca.* $1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the addition process. If, on the other hand, hydrogen atom abstraction occurs from **2** rather than acetonitrile, the rate constant for the addition could be as high as 10^7 or even $10^8 \text{ M}^{-1} \text{ s}^{-1}$! However, the measured rate constant (k_1) could be that of the addition process since this reaction seems to be at least as fast as hydrogen atom abstraction.

Note that it cannot be ruled out that products **18** and **20** arise from reaction of **8**^{•-} with acetonitrile. This reaction, however, should also be governed by spin density (radical) rather than charge density (ionic). Another possible pathway could involve reduction of *p*-cyanophenyl radical by **8**^{•-} to give the *p*-cyanophenyl anion. This anion could then attack acetonitrile. Recently, Arnold *et al.*^{13a} found that irradiation of an acetonitrile-methanol solution of **8** and 2-methylhexa-1,5-diene or **8** and 2,5-dimethylhexa-1,5-diene resulted in the formation of imines. The involvement of radical intermediates was considered but based on calculated (STO-3G) spin and charge densities in **8**^{•-} (Fig. 2; Table 4) it was concluded that reduction of the intermediate radical to the anion and subsequent attack on **8** was a more plausible mechanism. However, reduction of the *p*-cyanophenyl radical would generate the *p*-cyanophenyl anion, an extremely strong base and benzonitrile (**18**) rather

than *p*-cyanoacetophenone (**20**) would be observed. The product ratio (**18**:**20** = 1:4) that was observed does not comply with that mechanism.

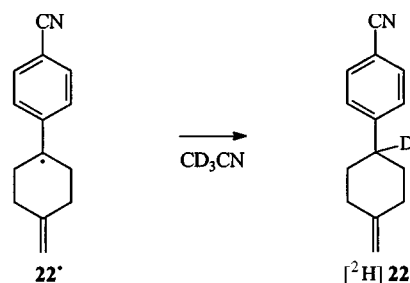
An intramolecular radical addition to a nitrile group can be used to explain the formation of 5'-methyl-4-methylene-4'-oxospiro[cyclohexane-1,3'-pyrrole] (**21**). The sequence of events involves addition of acetonitrile to **2**^{•+} followed by attack of cyanide ion on the intermediate radical cation, intramolecular radical addition to the carbon of the nitrile (a 1,5-*exo* cyclization), followed by hydrolysis (Scheme 7).



Scheme 7

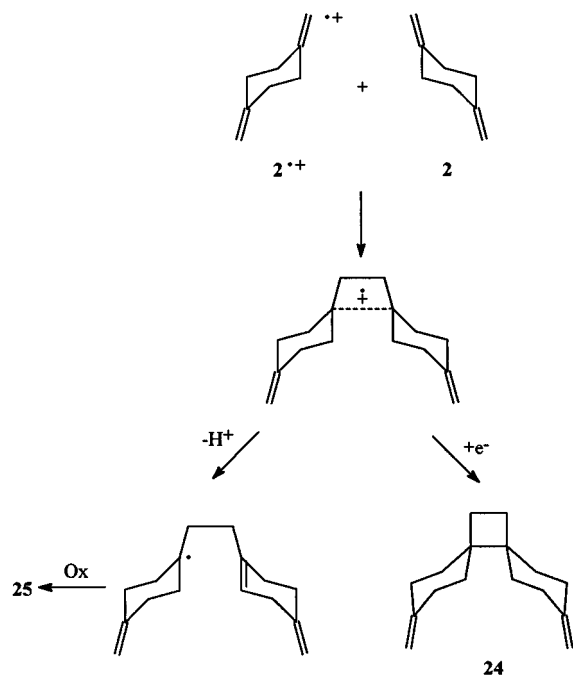
Another possible pathway could be reduction of the radical followed by nucleophilic attack on the carbon of the nitrile and hydrolysis of the imine. From the data available here it is not possible to distinguish between these two pathways. However, note that reduction of a tertiary alkyl radical by **8**^{•-} is usually an endergonic reaction.

The formation of 4-(4-cyanophenyl)-1-methylenecyclohexane (**22**) remains unexplained. From experiments performed in CD₃CN it is evident that deuterium is incorporated and therefore it is likely that radical **22**[•] is an intermediate (Scheme 8). It is, however, unclear how this intermediate is formed from **2**.



Scheme 8

Dimerization products are commonly observed in radical ion reactions.²³ The mechanism of this type of reaction is thought to be either a stepwise or a concerted mechanism. There is evidence for both mechanisms but the concerted mechanism giving a long-bond cyclobutane intermediate is favoured. We can assume that the two isolated dimerization products from this reaction {4,4'-bis(methylene)dispiro[cyclohexane-1,1'-cyclobutane-2',1''-cyclohexane] (**24**) and 1-(4-methylbenzene)-2-(1-methylene-4-cyclohexyl)ethane (**25**)} stem from the same radical cation intermediate. This intermediate then undergoes a ring closure reaction to yield **24** or a deprotonation (plus additional oxidation steps) to give **25** (Scheme 9).



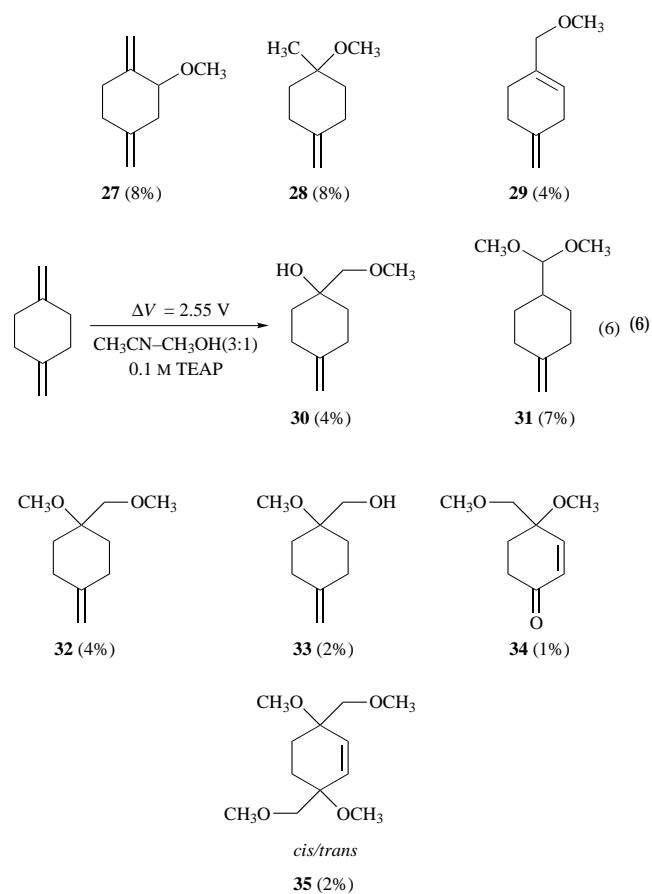
Scheme 9

Electrochemical oxidation of 1,4-bis(methylene)cyclohexane (2) in the presence of a nucleophile

There are several reports in the literature concerning the anodic oxidation of alkenes in the presence of a nucleophile.²⁴ For example, the electrochemical oxidation of cyclic alkenes (cyclohexene, methylcyclohexenes and cyclopentene) in the presence of methanol yielded allylic-substituted products.^{24a} In the case of cyclohexene a rearranged disubstituted product [bis(methoxymethyl)cyclopentane] was also observed. The electrochemical oxidation of α - and β -pinene in methanol gave only ring-opened products. This is in good agreement with the studies of the photo-NOCAS reaction on these species,^{10c} indicating that in these photochemical and electrochemical reactions the same intermediates are involved. The initially formed radical cation is a ring closed species, but its lifetime is too short to be trapped by the nucleophile. In their electrochemical oxidation studies of non-conjugated dienes,^{24b} Shono *et al.* found that several dienes showed transannular interaction. For example, electrooxidation of norbornadiene and bicyclo[2.2.2]octadiene gave cyclized products, whereas limonene and 4-vinylcyclohexene did not.

Performing a controlled potential electrolysis experiment on **2** (0.1 M) in acetonitrile–methanol (3:1) (0.1 M TEAP) at 2.55 V [$E_1^{ox}(\mathbf{2}) = 2.49$ vs. SCE; Table 1] resulted in the formation of several products [reaction (6)]. None of these products give any indication of transannular interaction in $2^{\cdot+}$.

The products can be divided into three categories: mono substitutions or additions, double substitutions or additions and multiple substitutions or additions. The first group consists of 2-methoxy-1,4-bis(methylene)cyclohexane (**27**), 4-methoxy-4-methyl-1-methylenecyclohexane (**28**) and 1-(methoxymethyl)-4-methylenecyclohex-1-ene (**29**). These products account for 50% of the total yield based on the initial amount of **2** present. The second group includes 1-(methoxymethyl)-4-methylenecyclohexanol (**30**), 4-(dimethoxymethyl)-1-methylenecyclohexane (**31**), 4-methoxy-4-(methoxymethyl)-1-methylenecyclohexane (**32**) and (1-methoxy-4-methylenecyclohexyl)methanol (**33**). The sum of these four compounds accounts for 42% of the total yield. Two of the products (8% of the total yield) can be placed in the last group: 4-methoxy-4-(methoxymethyl)-cyclohex-2-en-1-one (**34**) and 3,6-dimethoxy-3,6-bis(methoxymethyl)cyclohex-1-ene (**35**). This last compound (**35**) was isolated as a mixture of diastereomers. All but four (**27**, **28**, **34** and



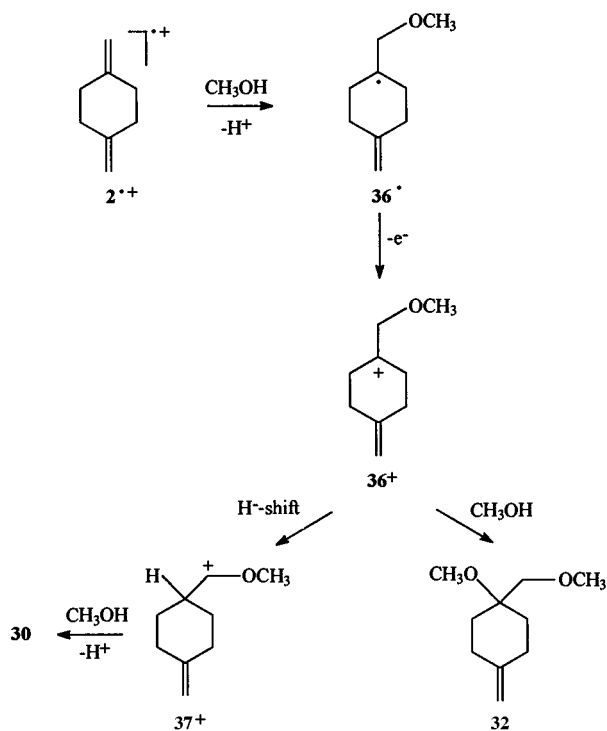
35) of the products are a result of a one-electron oxidation of one of the double bonds, followed by nucleophilic (methanol or water \ddagger) attack. After deprotonation of the distonic radical cation the intermediate radical is further oxidized to the cation followed by deprotonation (to give an alkene) or a second nucleophilic attack. Products **27** and **29** are typical allylic substitution products, however, **27** can only be formed by deprotonation of the radical cation ($2^{\cdot+}$). The resulting allylic radical is further oxidized to the carbocation which undergoes nucleophilic attack at C-2.

It is clear that several deprotonation steps take place and that the acidity of the solution will increase. Methanol will, in general, serve as the base but the double bonds in **2** can also serve as the base. Protonation of **2** leads to the stable tertiary carbocation (2^+) which will then undergo nucleophile attack. Examination of the product mixture shows that only **28** may have arisen from this type of 'acid-catalysis'. In a control experiment in which **2**, dissolved in an acetonitrile–methanol (3:1) mixture, was treated with concentrated sulfuric acid, several products were formed but only **28** was present in both (acid-catalysed and electrochemical) reaction mixtures.

Products **30–33** are the result of a second nucleophilic addition. The important intermediate is the carbocation 36^+ which is a result of an oxidation of the initially formed radical (36^{\cdot}). Nucleophilic (methanol or water) attack at C-4 will give products **30**, **32** and **33**. Product **31** is formed following a hydride transfer from C-8 to C-4 and subsequent nucleophilic attack on C-8 (Scheme 10). The relative yields (**31**, 7%; **30–32** combined: 10%) suggest that this hydride shift is a facile process. This is not surprising since the positive charge in 37^+ is stabilized by the adjacent oxygen.

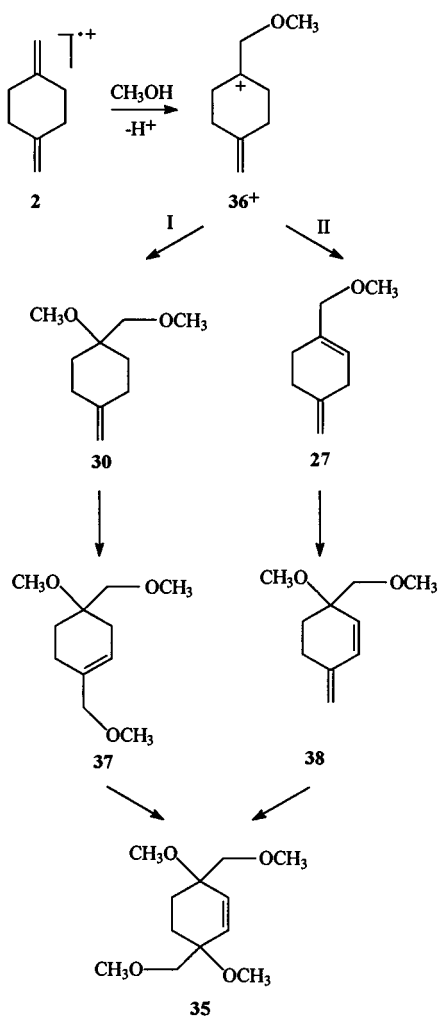
Formation of **34** and **35** involves a more complicated process. There are two possible pathways that lead toward product **35**.

\ddagger Although care was taken to exclude water, this possibility cannot be ruled out. Sources are likely to be acetonitrile and the electrolyte tetraethylammonium perchlorate, which was recrystallized from water.



Scheme 10

Pathway I involves subsequent oxidation of both double bonds and a deprotonation in the final step. Pathway II involves oxidation of the first double bond, deprotonation to give a conjugated diene which is then further oxidized (Scheme 11).



Scheme 11

Pathway I involves intermediate **37**, which resembles the isolated product **29**; however, **37** was not isolated from the reaction mixture. The conjugated diene **38** (an intermediate in pathway II) is likely to be very reactive under these (oxidative) conditions and **35** will be formed rapidly. The presence of **34** is also an indication that **38** is an intermediate. Compound **34** results from **38** as well; however, the nucleophile in this case is water and several subsequent deprotonation steps lead to the ketone.

The overall electrooxidation of **2** in an acetonitrile–methanol (3:1) solution is a two-electron process. This number can be derived using the total amount of current that was consumed in this reaction (3800 C) and the conversion of **2**, as determined by calibrated GC-FID [eqn. (7)], where n is the number

$$n = (QM)/(aF) \quad (7)$$

of electrons involved in the oxidation process per molecule substrate, Q is the total amount of Coulombs consumed, M is the molecular weight of the substrate, a is the amount of substrate that has been converted (in grams) and F is Faraday's constant.

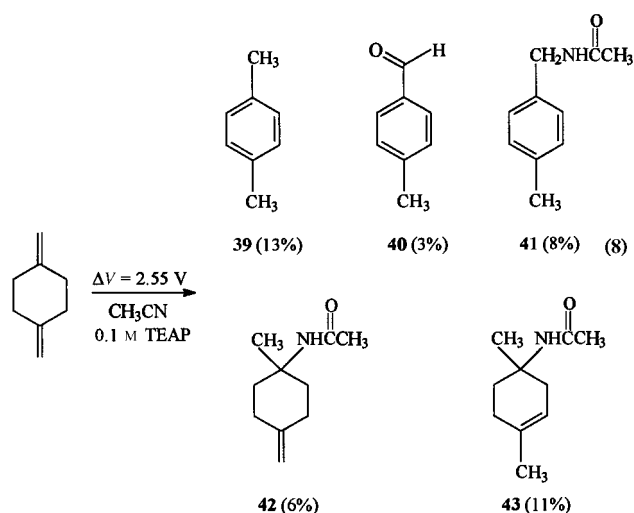
Using calibrated GC-FID, the conversion of **2** was determined to be 86%, *i.e.* $a = 2.15$ g. From eqn. (7) we then obtain a value for n of 2.0. This is consistent with the observed product mixture. Formation of products **27**, **29**, **30–33** each requires 2 oxidation steps. These compounds account for *ca.* 75% of the total yield. The formation of **34** and **35** requires more oxidation steps, but this is compensated for by product **28** which only requires one oxidation step. As mentioned above, compound **28** can be formed by protonation of the methylene group by $2^{\bullet+}$ (or indirectly by CH_3OH_2^+). In order for one molecule of **28** to be formed, one molecule of **2** needs to undergo a one-electron oxidation. This leaves 2^{\bullet} , an allylic radical, which will undergo a second oxidation, followed by nucleophilic attack to give **27** and **29**.

Electrochemical oxidation of 1,4-bis(methylene)cyclohexane (**2**) in the absence of a nucleophile

The results discussed above clearly show that following formation of the radical cation, nucleophilic attack is very rapid and there is no evidence for rearrangements, cyclization or bond cleavage. Extending the lifetime of the radical cation by inhibiting nucleophilic attack might lead to different reactions. With this in mind the electrochemical oxidation of **2** was carried out in the absence of a nucleophile (methanol). Three of the isolated products, 1,4-dimethylbenzene (**39**), 4-methylbenzaldehyde (**40**) and *N*-(4-methylbenzyl)acetamide (**41**), are the result of multiple oxidation leading to aromatic molecules. The other two products, *N*-(1-methyl-4-methylenecyclohexyl)acetamide (**42**) and *N*-(1,4-dimethylcyclohex-3-enyl)acetamide (**43**), have the cyclohexyl moiety (partially) intact [reaction (8)]. Analysis of the reaction mixture with GC-MS indicated the presence of several other products with m/z 108. These are thought to be isomeric dimethylcyclohexadienes.

The formation of aromatic products upon electrochemical oxidation is a well known phenomenon.^{24a,25} These products are usually explained on the basis of the mechanism of the Ritter reaction, *i.e.* cationic intermediates are formed. The initial step is formation of the radical cation $2^{\bullet+}$. This species is highly acidic and, in the absence of a nucleophile, will rapidly deprotonate. Both acetonitrile and **2** can serve as the base; protonating **2** leads to the formation of a stable (tertiary) carbocation and the allylic radical. The carbocation then is deprotonated (by acetonitrile or **2**) to give a diene. The oxidation potential of the diene is lower than that of the alkene and further oxidation is facile. This sequence is repeated until an aromatic product is obtained. The product at this stage is 1,4-dimethylbenzene (**39**), one of the major constituents of the reaction mixture [reaction (8)].

The reaction does not necessarily stop at this point. Aromatic



compounds undergo anodic oxidation as well; often this involves substitution of the side-chain. For example, oxidation of polymethylbenzenes in acetonitrile leads to *N*-substituted acetamides.²⁵ Product **41** obviously is a secondary product arising from the oxidation of **39** with acetonitrile acting as the nucleophile (another nucleophile, water, is also necessary for the formation of the acetamides). Oxidation of **39** also leads to **40**, but in this case water is the initial nucleophile reacting with the benzylic cation.

The aliphatic products **42** and **43** are formed by nucleophilic attack of acetonitrile on the tertiary carbocation formed by protonation of **2** (by **2**^{•+} and/or CH₃CNH⁺). Another control experiment showed that this is indeed the case. Reaction of **2** in acetonitrile with concentrated sulfuric acid resulted in the formation of three products (**39**, **42** and **43**) in a ratio of 10:5:1.

The ratio of the products (**39** + **40**):(**41** + **42** + **43**) obtained from reaction (8) indicates that, under these reaction conditions, deprotonation is *ca.* 1.4 times as fast as nucleophilic attack. Radical cations are known to have much lower p*K*_a values than their neutral precursors, *i.e.* they are strong acids.²⁶ Deprotonation of the radical is therefore expected to be a fast process. Since the ratio of (deprotonation/nucleophilic attack) is only 1.4 this must mean that acetonitrile, under these conditions, is also an effective nucleophile.

After 21 days only 2047 C had been consumed in this reaction. However, the conversion of **2** at this point is 87% (calibrated GC-FID); *i.e.* the reaction is quite efficient. Using eqn. (7), we find that *n* = 1.1. Again, this is consistent with the observed products and the mechanisms proposed for their formation. At first glance the formation of aromatic compounds looks like a six-electron oxidation process. However, as discussed above, the aromatic compounds result from the Ritter reaction which involves carbocations. One-electron oxidation of **2** leads to the radical cation (**2**^{•+}) which will deprotonate to another molecule of **2**. This sequence of oxidation-deprotonation can continue until aromatic products are formed. Overall, a one-electron oxidation (*n* = 1) reaction is the result.

Conclusions

Two major reaction pathways for the radical cation of 1,4-bis(methylene)cyclohexane (**2**^{•+}) have been identified by studying the photoinduced electron transfer and the electrochemical oxidation of **2**. The behaviour of the radical cation was studied both with and without the nucleophile present. While the photochemical and electrochemical experiments yield different products, the major reaction pathways of **2**^{•+} in these experiments are understandably similar. In the presence of a good nucleophile the products arise from nucleophilic attack on the radical cation. This is the case in both the photochemical and

the electrochemical experiments. In the absence of a nucleophile, the electrooxidation experiments show that there is a preference for deprotonation. However, the solvent that was used in this experiment (acetonitrile) can and does act as a nucleophile resulting in the formation of *N*-acetamides. It was shown using a control experiment that these products arise from Ritter-type reactions, *i.e.* the intermediates are carbocations. This is not surprising since the radical cations are highly acidic species and deprotonation of **2**^{•+} leads (directly or indirectly) to **2**⁺. The photoinduced electron transfer experiments in the absence of a nucleophile leads to the formation of some interesting products, including two dimeric species (**24** and **25**). Another interesting observation is the presence of *p*-cyanoacetophenone (**20**), which is thought to arise by addition of *p*-cyanophenyl radical to acetonitrile, followed by hydrolysis.

The differences observed between the electrochemical and the photochemical reactions are most likely due to the fact that in the electrochemical experiments the initially formed radical cation (**2**^{•+}) is close (or adsorbed) to the electrode and a second oxidation of the resulting radical (formed after deprotonation or nucleophilic attack) is therefore often inevitable.

The previous calculations, summarized in Scheme 1, have indicated that 1,4-bis(methylene)cyclohexane (**2**) and its radical cation (**2**^{•+}) are the most stable of the C₈H₁₂ and C₈H₁₂^{•+} isomers considered. This study therefore provides the foundation for future characterization of the higher energy isomers which we expect/predict will dimerize, rearrange, cyclize or fragment to some of the same intermediates observed in this study. These studies are currently underway.

Experimental

General information

¹H and ¹³C NMR spectra were obtained on a Bruker 250 MSL spectrometer. Spectra were recorded in parts per million and frequencies are relative to tetramethylsilane; *J* values are given in Hz. IR spectra were recorded on a Nicolet 205 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, B.C. Exact mass determinations were obtained using a GEC 21-110B spectrometer. Melting points were determined using a Cybron Corporation Thermolyne apparatus with a digital thermocouple and are corrected. Product yields were determined using a Hewlett-Packard (HP) 5890 gas chromatograph with a DB-1701 fused silica WCOT column (30 m × 0.25 mm, 0.25 μm film thickness) and a calibrated flame ionization detector (GC-FID) and, for consistency, are based upon 1,4-bis(methylene)cyclohexane (**2**). An HP 3392A integrator was interfaced with the GC-FID to obtain peak areas. An HP 5890 gas chromatograph with a 5% phenyl methyl silicone fused silica WCOT column (25 m × 0.20 mm, 0.33 μm film thickness) interfaced with an HP 5970 mass selective detector (GC-MS) was also used for product analyses. Mass spectra are reported as *m/z* (relative intensity). Separation of product mixtures was generally carried out using preparative medium-pressure liquid chromatography (MPLC), followed by dry column flash chromatography (DCFC)²⁷ and preparative GC. The MPLC consists of a 2.5 cm × 1 m column packed with thin-layer chromatography (TLC) grade silica gel (Rose Scientific Ltd., Silica Gel G/UV-254 with Gypsum binder, cat. no. 81632) at a pressure of 28 psi using helium (1 psi = 6.9 kPa). Connected to the MPLC was a UV spectrophotometer-fraction collector that collects *ca.* 10 ml fractions. For DCFC the column was packed with thin-layer chromatography grade silica gel (Rose Scientific Ltd., Silica Gel G/UV-254 with Gypsum binder, cat. no. 81632). Fraction sizes were *ca.* 5 ml. Preparative gas chromatography was carried out using a Varian Aerograph 920 equipped with a 20% SE-30 on Chromosorb W 60/80 column (6' × 1/4").

Materials

Acetonitrile (Fisher ACS grade) was distilled twice, first from

sodium hydride and then from phosphorus pentoxide. It was then passed through a column of basic alumina, refluxed over calcium hydride for 24 h (under a nitrogen atmosphere), fractionally distilled (under nitrogen) and stored over molecular sieves (3 Å).²⁸ Anhydrous acetonitrile (Aldrich) was stored over molecular sieves (3 Å) upon arrival and used without further purification. Methanol was distilled and then stored over molecular sieves (3 Å). Anhydrous methanol (Aldrich) was stored over molecular sieves (3 Å) upon arrival and used without further purification. 1,4-Dicyanobenzene (**8**) (Aldrich) was purified by treatment with Norite in methylene chloride, followed by recrystallization from 95% ethanol. Biphenyl (**9**) (Eastman Kodak) was recrystallized from methanol. Tetraethylammonium perchlorate (TEAP) (Fisher) was recrystallized three times from water and then dried in a vacuum oven for 15 h, 70 °C, 0.25 Torr (1 Torr = 133.3 Pa). 1,4-Bis(methylene)cyclohexane, 99% (**2**) was purchased from Wiley Organics and used without further purification.

Irradiation

Irradiations were generally carried out on solutions of acetonitrile–methanol (3:1) with 1,4-dicyanobenzene, the alkene with or without a co-donor. In certain experiments methanol was omitted. Solutions were irradiated in either 2 cm id Pyrex tubes or 5 mm Pyrex NMR tubes, which were degassed by nitrogen ebullition. The samples were irradiated at 10 °C using a CGE 1 kW medium-pressure mercury vapour lamp contained in a water-cooled quartz immersion well.

Cyclic voltammetric measurements

Cyclic voltammetry at a sweep rate of 100 mV s⁻¹ was used to obtain the oxidation potential of the alkene. The apparatus has been described.²⁹ The working electrode was a platinum sphere (1 mm diameter) and the counter electrode was a platinum wire. The reference electrode was a saturated calomel electrode (SCE), which was connected to the solution (TEAP 0.1 M, acetonitrile) through a Luggin capillary. The alkene concentration was *ca.* 0.005 M. Since the anodic wave was irreversible, the half-wave potential was taken as 0.028 V before the anodic peak potential.³⁰

Controlled potential electrolyses

Controlled potential electrolyses of **2** were performed with a customized two-electrode cell (total volume 200 ml), containing the working electrode and the reference electrode. The counter electrode compartment, containing the counter electrode, was fitted into the cell; the two compartments are connected by means of fine glass frit. Both the working electrode and counter electrode were platinum mesh (6.5 cm²). The reference electrode was the standard calomel electrode (SCE). All experiments were performed at room temperature.

The electrochemical measurements were obtained with a Princeton Applied Research (PAR) 173 potentiostat in combination with a PAR 175 universal programmer and a PAR 179 digital coulometer.

Irradiation of a mixture of 1,4-bis(methylene)cyclohexane (**2**) and 1,4-dicyanobenzene (**8**) in acetonitrile–methanol (3:1)

A mixture of 1,4-bis(methylene)cyclohexane (**2**) (2.2 g, 2.0 × 10⁻² mol) and 1,4-dicyanobenzene (**8**) (1.3 g, 1.0 × 10⁻² mol) dissolved in 200 ml acetonitrile–methanol (3:1) was irradiated for 12 days. The solvent was removed by rotary evaporation and the residue was chromatographed on silica gel (MPLC) using a linear solvent gradient [hexanes–(50% diethyl ether–50% hexanes)]. Compound **16** was further purified by preparative GC.

4-(Methoxymethyl)-1-methylenecyclohexane (16). ν (liquid film)/cm⁻¹ 3071 (w), 2981 (m), 2923 (s), 2854 (s), 2809 (w), 1650 (m), 1448 (m), 1387 (w), 1212 (w), 1195 (w), 1124 (s), 1102 (s), 966 (w), 944 (w) and 888 (s); δ_{H} (CDCl₃, AC250) 4.59 (s, 2H),

3.31 (s, 3H), 3.18 (d, 6.71, 2H), 2.29 (d, 13.43, 2H), 2.01 (td, 4.27, 13.43, 2H), 1.87–1.80 (m, 2H), 1.77–1.63 (m, 1H), 1.04 (qd, 4.27 and 12.20, 2H); δ_{C} (CDCl₃, AC250) 149.53 (s), 106.92 (t), 78.05 (t), 58.81 (q), 37.53 (d), 34.14 (t) and 31.16 (t); m/z 140 (M⁺, 1%), 108 (38), 93 (100), 91 (25), 80 (47), 79 (67), 77 (25), 67 (40), 55 (21) and 53 (25).

4-(4-Cyanophenyl)-4-(methoxymethyl)-1-methylenecyclohexane (17). ν (liquid film)/cm⁻¹ 3071 (m), 2981 (m), 2933 (s), 2875 (s), 2228 (s), 1651 (m), 1607 (m), 1506 (m), 1450 (m), 1404 (w), 1382 (w), 1191 (m), 1116 (s), 979 (w), 958 (w), 892 (m) and 836 (m); δ_{H} (CDCl₃, AC250) 7.63 (d, 8.54, 2H), 7.51 (d, 8.54, 2H), 4.61 (s, 2H), 3.31 (s, 2H), 3.17 (s, 3H), 2.23–2.17 (3 line multiplet, 6.11, 10.37, 4H), 2.09–1.97 (m, 2H) and 1.83–1.66 (m, 2H); δ_{C} (CDCl₃, AC250) 150.09 (s), 148.07 (s), 132.02 (d), 128.10 (d), 119.10 (s), 109.81 (s), 107.50 (t), 81.53 (t), 59.43 (q), 43.31 (s), 33.75 (t) and 30.63 (t); m/z 241 (M⁺, 6%), 209 (51), 196 (41), 195 (21), 181 (25), 180 (25), 168 (19), 154 (51), 142 (21), 140 (19), 117 (19), 116 (100), 115 (21), 93 (38), 89 (19), 79 (21), 77 (23) and 67 (41) (Calc. for C₁₆H₁₉NO: C, 79.63; H, 7.94; N, 5.80. Found: C, 78.75, 80.28; H, 7.85, 7.89; N, 5.75, 5.91).

Irradiation of a mixture of 1,4-bis(methylene)cyclohexane (**2**) and 1,4-dicyanobenzene (**8**) in acetonitrile–methan[²H]ol (3:1)

A mixture of 1,4-bis(methylene)cyclohexane (**2**) (0.0440 g, 4.1 × 10⁻⁴ mol) and 1,4-dicyanobenzene (**8**) (0.0365 g, 2.9 × 10⁻⁴ mol) dissolved in 4 ml acetonitrile–methan[²H]ol (3:1) was irradiated for 6 h. Deuterium incorporation was checked by GC–MS analysis. Identification of the products was based on the mass spectra and the retention times (GC–MS and GC–FID) of the compounds.

Irradiation of a mixture of 1,4-bis(methylene)cyclohexane (**2**), 1,4-dicyanobenzene (**8**) and biphenyl (**9**) in acetonitrile

A solution of 1,4-bis(methylene)cyclohexane (**2**) (2.3 g, 2.1 × 10⁻² mol), 1,4-dicyanobenzene (**8**) (2.6 g, 2.0 × 10⁻² mol) and biphenyl (**9**) (3.1 g, 2.0 × 10⁻² mol) in 200 ml acetonitrile was irradiated for 41 days. The solvent was removed by rotary evaporation and the residue was chromatographed on silica gel (MPLC) using a linear solvent gradient (hexanes–diethyl ether). Mixtures of compounds were further purified by DFC using cyclohexane or a cyclohexane–5% diethyl ether–95% cyclohexane gradient.

Benzonitrile (18). This compound was not isolated, but identification is based on its mass spectrum: m/z 103 (M⁺, 100%), 77 (12), 76 (82), 75 (23), 74 (12), 64 (4), 63 (8), 62 (4), 52 (14) and 51 (27); retention time (GC–FID and GC–MS) and the mass spectrum were compared to that of an authentic sample (Aldrich).

4-Cyanotoluene (19). Identification of this compound is based on its mass spectrum: m/z 117 (M⁺, 100%), 116 (76), 91 (12), 90 (50), 89 (39), 76 (5), 75 (7), 64 (11), 63 (24), 62 (12) and 51 (12); retention time (GC–FID and GC–MS) and mass spectrum were compared to that of the pure compound (Aldrich).

4-Cyanoacetophenone (20). δ_{H} (CDCl₃, AC250) 8.05 (d, 8.54, 2H), 7.78 (d, 8.54, 2H), 2.65 (s, 3H); δ_{C} (CDCl₃, AC250) 196.50 (s), 139.82 (s), 132.45 (d), 128.63 (d), 117.88 (s), 116.31 (s) and 26.72 (q); m/z 145 (M⁺, 16%), 130 (100), 102 (57), 76 (12), 75 (19), 74 (6), 63 (4), 62 (3) and 51 (15); retention time (GC–FID and GC–MS) and the mass spectrum were compared to that of an authentic sample (Aldrich).

5'-Methyl-4-methylene-4'-oxospiro[cyclohexane-1,3'-pyrrolin]e (21). ν (CDCl₃)/cm⁻¹ 3098 (m), 3054 (m), 2930 (s), 2854 (m), 1728 (s), 1681 (w), 1651 (m), 1501 (m), 1442 (m), 1405 (w), 1377 (w), 1345 (w), 1276 (w), 1197 (w), 1115 (w), 1022 (w) and 841 (s); δ_{H} (CDCl₃, AC250) 4.72 (s, 2H), 4.16–4.10 (m, 2H), 2.47–2.38 [dt (unresolved), observed splittings: 3.67, 4.27, 13.43, 14.04, 2H], 2.15 (t, 2.44, 3H), 2.16–2.05 (td, partially under triplet at 2.15 ppm, 4.88, 13.43, 2H), 1.67–1.56 [td (unresolved), observed splittings: 4.27, 12.20, 12.82, 2H] and 1.50–1.41 (m, 2H); δ_{C} (CDCl₃, AC250) 206.79 (s), 170.91 (s), 146.16 (s), 108.64

(t), 67.13 (t), 45.73 (s), 33.75 (t), 31.25 (t) and 13.95 (q); m/z 177 (M^+ , 6%), 108 (83), 93 (100), 91 (33), 80 (32), 79 (61), 78 (11), 77 (30), 67 (12), 65 (12), 55 (13), 54 (16) and 53 (18).

4-(4-Cyanophenyl)-1-methylenecyclohexane (22). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3070 (w), 2979 (w), 2930 (s), 2856 (m), 2228 (s), 1650 (m), 1607 (m), 1505 (m), 1444 (m), 1410 (w), 1180 (w), 1079 (w), 978 (w), 893 (s) and 838 (s); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 7.57 (d, 7.93, 2H), 7.30 (d, 7.93, 2H), 4.70 (s, 2H), 2.79–2.67 (m, 1H), 2.46–2.41 (m, 2.44, 11.59, 2H), 2.24–2.13 (m, 2H), 1.97 (d, 12.82, 2H) and 1.61–1.44 [qd (unresolved), observed splittings: 3.67, 4.27, 12.21, 12.81, 2H]; $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 152.22 (s), 147.72 (s), 131.62 (d), 127.61 (d), 119.02 (s), 109.72 (s), 107.95 (t), 44.17 (d), 34.91 (t) and 34.71 (t); m/z 197 (M^+ , 60%), 182 (33), 168 (81), 155 (37), 142 (21), 129 (61), 116 (38), 103 (17), 89 (21), 79 (40), 68 (100) and 53 (35) (M^+ , 197.1202. $\text{C}_{14}\text{H}_{15}\text{N}$ requires M , 197.1204).

2-(4-Cyanophenyl)-1,4-bis(methylene)cyclohexane (23). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3075 (w), 2982 (w), 2937 (s), 2847 (m), 2227 (s), 1651 (m), 1607 (m), 1504 (w), 1442 (m), 1410 (w), 899 (s) and 845 (s); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 7.61 (d, 7.94, 2H), 7.36 (d, 8.54, 2H), 4.83 (s, 1H), 4.81 (s, 1H), 4.79 (s, 1H), 4.23 (s, 1H), 3.44 (t, 7.32, 1H), 2.55 (d, 7.93, 2H), 2.46–2.38 (m, 2H) and 2.19–2.28 (m, 2H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 149.94 (s), 148.24 (s), 146.29 (s), 132.00 (d), 129.14 (d), 119.01 (s), 110.21 (t), 110.14 (s), 109.80 (t), 50.19 (d), 40.75 (t), 35.84 (t) and 35.67 (t); m/z 209 (M^+ , 53%), 194 (13), 180 (15), 166 (19), 153 (21), 140 (26), 127 (21), 116 (22), 102 (74), 93 (100), 91 (32), 80 (56), 77 (38), 63 (15) and 51 (20) (M^+ , 209.1194. $\text{C}_{15}\text{H}_{15}\text{N}$ requires M , 209.1204).

4,4'-Bis(methylene)dispiro[cyclohexane-1,1'-cyclobutane-2,2'-cyclohexane] (24). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3071 (w), 2927 (s), 2855 (s), 1652 (w), 1458 (m), 1376 (w) and 886 (m); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 4.56 (s, 4H), 2.24–1.94 (m, 8H), 1.84–1.71 (m, 8H) and 1.74 (s, 4H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 150.04 (s), 105.89 (t), 42.76 (s), 33.87 (t), 29.71 (t) and 26.43 (t); m/z 216 (M^+ , 2%), 201 (3), 160 (8), 120 (7), 109 (25), 108 (24), 106 (61), 93 (100), 91 (42), 79 (71), 77 (36), 67 (31) and 53 (21).

1-(4'-Methylphenyl)-2-(4'-methylenecyclohexyl)ethane (25). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3064 (m), 3034 (m), 2927 (s), 2854 (m), 1481 (m), 1431 (m), 1078 (w) and 908 (s); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 7.07 (s, 4H), 4.59 (s, 2H), 2.59 (t, 7.93, 2H), 2.31 (s, 3H), 2.26 (s, 2H), 2.10–1.93 (m, 2H), 1.93–1.80 (m, 2H), 1.53 (s, 2H) and 1.25 [br s, 3H ($\text{CH}_2 + \text{CH}$)]; $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 150.02 (s), 139.85 (s), 134.98 (s), 128.95 (d), 128.17 (d), 106.55 (t), 38.61 (t), 36.70 (d), 34.56 (t), 34.33 (t), 32.89 (t), 29.69 (t) and 20.97 (q); m/z 214 (M^+ , 20%), 157 (6), 143 (5), 119 (11), 118 (58), 105 (100), 91 (24), 79 (25), 77 (24), 67 (19) and 53 (12).

Analysis of the mixture by GC–MS also indicated the presence of 1,2-bis(4'-cyanophenyl)ethane: m/z 232 (M^+ , 29%), 141 (100), 115 (28), 91 (9), 77 (3), 65 (7) and 51 (5).

Irradiation of a mixture of 1,4-bis(methylene)cyclohexane (2), 1,4-dicyanobenzene (8) and biphenyl (9) in [$^2\text{H}_3$]acetonitrile

A solution of 1,4-bis(methylene)cyclohexane (2) (0.0110 g, 1.0×10^{-4} mol), 1,4-dicyanobenzene (8) (0.0085 g, 6.6×10^{-5} mol) and biphenyl (9) (0.0074 g, 4.8×10^{-5} mol) in 1 ml [$^2\text{H}_3$]acetonitrile was irradiated for 5 days. Deuterium incorporation was checked by GC–MS analysis. Identification of the products was based on the mass spectra and the retention times (GC–MS and GC–FID) of the compounds.

Reaction of phenyl radical with acetonitrile: formation of acetophenone

A solution of dibenzoyl peroxide (0.025 g, 1.0×10^{-4} mol) in 25 ml acetonitrile was refluxed for 1 h. Analyses of the reaction mixture by GC–MS and GC–FID at several intervals revealed the presence of acetophenone in trace amounts. The major products are benzoic acid, biphenyl and phenyl benzoate. Identification of acetophenone rests on its mass spectrum (GC–MS) and retention times (GC–FID and GC–MS) all of which were compared to those of an authentic sample (Fisher).

Electrolysis of a solution of 1,4-bis(methylene)cyclohexane (2) in acetonitrile–methanol (3:1)

A solution of tetraethylammonium perchlorate (TEAP) (4.6 g, 0.1 M) in 200 ml acetonitrile–methanol (3:1) was degassed by nitrogen ebullition for 30 min. After this period 1,4-bis(methylene)cyclohexane (2) (2.5 g, 2.3×10^{-2} mol) was added to the solution and the mixture was electrolysed ($\Delta V = 2.55$ V) for 75 h at room temperature. During this period 3800 C were consumed. The solvent was evaporated and the residue was chromatographed on silica gel (MPLC) using hexanes. Further purification of the products and mixtures was achieved by preparative GC.

2-Methoxy-1,4-bis(methylene)cyclohexane (27). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3079 (m), 2979 (m), 2938 (s), 2855 (m), 2825 (m), 1654 (m), 1446 (m), 1095 (s), 901 (s), 842 (m), 746 (s) and 712 (w); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 4.93 (s, 2H), 4.79 (d, 6.71, 2H), 3.69 [dd (unresolved), observed splittings: 4.27 and 4.88, 1H], 3.26 (s, 3H), 2.42 (d, 4.27, 2H), 2.35–2.26 (m, 2H), 2.19–2.14 (m, 2H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 146.60 (s), 144.63 (s), 110.48 (t), 110.36 (t), 81.66 (d), 56.00 (q), 41.95 (t), 35.67 (t) and 31.83 (t); m/z 138 (M^+ , 23%), 123 (15), 106 (44), 93 (27), 91 (100), 79 (51), 77 (36), 71 (19), 67 (27), 55 (25) and 53 (30).

4-Methoxy-4-methyl-1-methylenecyclohexane (28). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 2924 (s), 2853 (m), 1737 (m), 1649 (w), 1462 (w), 1078 (w), 912 (w), 886 (w) and 743 (m); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 4.61 (s, 2H), 3.21 (s, 3H), 2.36–2.24 [td (unresolved), observed splittings: 4.27, 4.88, 11.59, 12.21 and 13.43, 2H], 2.11–2.02 (dt, 4.27 and 13.43, 2H), 1.89–1.80 (m, 2H), 1.43–1.31 (m, 2H) and 1.13 (s, 3H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 148.90 (s), 106.78 (t), 72.85 (s), 48.60 (q), 36.91 (t), 30.44 (t) and 23.73 (q); m/z 140 (M^+ , 0.6%), 125 (21), 111 (35), 108 (76), 93 (100), 91 (29), 85 (15), 79 (41), 77 (29), 72 (24), 67 (32) and 55 (38).

1-(Methoxymethyl)-4-methylenecyclohex-1-ene (29). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3072 (w), 2982 (m), 2908 (s), 2843 (m), 2817 (m), 1654 (m), 1449 (m), 1378 (w), 1359 (w), 1278 (w), 1215 (w), 1193 (m), 1152 (m), 1102 (s), 1053 (w), 958 (w), 936 (w), 909 (m), 887 (s) and 815 (w); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 5.64 (s, 1H), 4.76 (s, 2H), 3.79 (s, 2H), 3.29 (s, 3H), 2.81 (s, 2H), 2.36–2.31 [3 line pattern (unresolved), observed splittings: 6.71 and 6.11, 2H], 2.16 (br d, 5.49, 2H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 145.45 (s), 134.91 (s), 123.87 (d), 107.85 (t), 76.62 (t), 57.60 (q), 33.23 (t), 31.42 (t) and 27.98 (t); m/z 138 (M^+ , 9%), 123 (5), 106 (36), 93 (30), 91 (100), 79 (32), 78 (52), 77 (46), 71 (23), 65 (20), 53 (18) and 51 (19) (M^+ , 138.1060. $\text{C}_9\text{H}_{14}\text{O}$ requires M , 138.1045).

1-(Methoxymethyl)-4-methylenecyclohexanol (30). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3438 (s), 3070 (w), 2979 (m), 2934 (s), 2891 (m), 2854 (m), 2827 (m), 1715 (w), 1683 (m), 1650 (m), 1445 (m), 1408 (w), 1372 (w), 1330 (w), 1273 (w), 1230 (w), 1195 (m), 1105 (s), 954 (m), 914 (s), 889 (m) and 745 (m); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 4.64 (s, 2H), 3.40 (s, 3H), 3.25 (s, 2H), 2.74–2.34 (m, 2H), 2.22 (s, 1H), 2.17–2.08 [dt (unresolved), observed splittings: 4.27, 4.88, 13.43 and 14.04, 2H], 1.79–1.71 (m, 2H) and 1.50–1.38 (m, 2H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 148.81 (s), 107.07 (t), 80.35 (t), 70.53 (s), 59.40 (q), 35.50 (t) and 30.04 (t); m/z 138 (8%), 111 (100), 106 (9), 93 (41), 91 (28), 81 (21), 77 (21), 69 (14), 67 (18), 55 (18) and 53 (17).

4-(Dimethoxymethyl)-1-methylenecyclohexane (31). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3071 (w), 2983 (m), 2936 (s), 2860 (m), 2832 (m), 1650 (m), 1445 (m), 1382 (m), 1249 (w), 1220 (w), 1186 (m), 1134 (s), 1102 (m), 1076 (s), 1054 (s), 1011 (w), 970 (m) and 891 (s); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 4.61 (3 line multiplet, 1.84 and 13.43, 2H), 4.02 (d, 7.32, 1H), 3.34 (s, 6H), 2.35–2.29 (m, 2H), 2.07–1.95 [dt (unresolved), observed splittings: 3.66, 4.27, 12.82 and 13.43, 2H], 1.94–1.83 (m, 2H), 1.82–1.68 (10 line pattern, 1H), 1.19–1.03 [qd (unresolved), observed splittings: 3.66, 4.27, 11.59, 12.21 and 12.82, 2H]; $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 149.14 (s), 107.99 (d), 106.92 (t), 53.52 (q), 39.63 (d), 34.98 (t) and 29.25 (t); m/z 170 (M^+ , 0.7%), 139 (7), 138 (6), 107 (16), 91 (15), 79 (25), 75 (100), 71 (23), 67 (13), 55 (13) and 53 (17).

4-Methoxy-4-(methoxymethyl)-1-methylenecyclohexane (32). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3071 (w), 2980 (m), 2934 (s), 2880 (s), 2829 (m),

1650 (m), 1457 (m), 1442 (m), 1196 (m), 1144 (m), 1103 (s), 1076 (s), 979 (w), 889 (m) and 734 (m); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 4.62 (s, 2H), 3.37 (s, 3H), 3.31 (s, 2H), 3.27 (s, 3H), 2.37–2.25 [td (unresolved), observed splittings: 3.66, 4.27, 12.20, 12.82 and 13.43, 2H], 2.13–2.04 (dt, 4.27 and 13.42, 2H), 1.94–1.86 (m, 2H), 1.44–1.32 [td (unresolved), observed splittings: 4.27, 4.88, 12.21, 12.82 and 13.43, 2H]; $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 148.75 (s), 106.89 (t), 76.06 (t), 74.41 (s), 59.36 (q), 49.21 (q), 32.20 (t) and 29.79 (t); m/z 142 (0.1%), 138 (1), 125 (100), 109 (4), 93 (62), 91 (38), 79 (13), 77 (32), 71 (7), 67 (17) and 53 (15).

(1-Methoxy-4-methylenecyclohexyl)methanol (33). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3447 (s), 3071 (w), 2936 (s), 1706 (m), 1651 (m), 1607 (w), 1459 (m), 1442 (m), 1072 (s), 1050 (s), 888 (s), 852 (m), 745 (m), 715 (m) and 671 (m); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 4.65 (s, 2H), 3.50 (s, 2H), 3.25 (s, 3H), 2.35–2.23 [td (unresolved), observed splittings: 4.27, 11.60 and 13.43, 2H], 2.17–2.08 (dt, 4.88 and 13.43, 2H), 1.76 (br s, 1H), 1.46–1.31 (m, 2H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 148.30 (s), 107.40 (t), 75.23 (s), 64.75 (t), 48.68 (q), 31.83 (t), 29.89 (t); m/z 125 (100%), 109 (2), 95 (5), 93 (49), 91 (30), 79 (8), 77 (24), 67 (13), 55 (7) and 53 (9).

4-Methoxy-4-(methoxymethyl)cyclohex-2-en-1-one (34). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 2936 (w), 2894 (w), 2831 (w), 1679 (s), 1455 (w), 1384 (w), 1199 (w), 1099 (w), 910 (s), 807 (w) and 734 (s); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 6.84 (d, 10.38, 1H), 6.12 (d, 10.37, 1H), 3.52 (s, 2H), 3.42 (s, 3H), 3.34 (s, 3H), 2.73–2.40 (m, 2H) and 2.32–2.04 (m, 2H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 198.83 (s), 150.15 (d), 131.93 (d), 75.88 (t), 74.74 (s), 59.64 (q), 51.30 (q), 34.41 (t) and 27.80 (t); m/z 170 (M^+ , 5%), 140 (7), 125 (100), 107 (8), 97 (54), 79 (23), 77 (17), 67 (25), 65 (14), 55 (16) and 53 (23) (M^+ , 170.0943). $\text{C}_9\text{H}_{14}\text{O}_3$ requires M , 170.0943.

3,6-Dimethoxy-3,6-bis(methoxymethyl)cyclohex-1-ene (35). A mixture of diastereomers was formed. $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 2980 (m), 2933 (s), 2887 (s), 2828 (s), 1686 (w), 1457 (m), 1394 (w), 1253 (w), 1196 (m), 1155 (w), 1105 (s), 1081 (s), 1007 (w), 961 (w), 913 (s), 879 (w), 781 (w) and 733 (s); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 5.89 (d, 8.54, 2H), 3.40 (s, 5H), 3.38 (s, 3H), 3.33 (s, 2H), 3.30 (s, 3H), 3.25 (s, 3H), 2.06–1.89 (m, 1H), 1.88–1.82 (m, 2H) and 1.75–1.61 (m, 1H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 133.65 (d), 133.46 (d), 77.03 (t), 76.93 (t), 75.26 (s), 74.45 (s), 59.66 (q), 59.52 (q), 50.91 (q), 50.56 (q), 25.32 (t) and 25.25 (t); m/z 185 (42%), 153 (42), 140 (16), 127 (14), 125 (35), 123 (18), 121 (100), 97 (17), 95 (15), 91 (16), 79 (12), 77 (16), 75 (20), 65 (10) and 53 (10) (M^+ – $\text{C}_2\text{H}_5\text{O}$, 185.1183). $\text{C}_{10}\text{H}_{17}\text{O}_3$ requires M , 185.1178).

Acid-catalysed reaction of 1,4-bis(methylene)cyclohexane in an acetonitrile–methanol (3:1) mixture

1,4-Bis(methylene)cyclohexane (**2**) (0.21 g, 1.9×10^{-3} mol) was dissolved in 16 ml of an acetonitrile–methanol (3:1) mixture and concentrated sulfuric acid (0.18 g, 1.8×10^{-3} mol) was added dropwise. The mixture was stirred for 24 h and the products were analysed by GC–MS and GC–FID. The identification of **28** was based on the mass spectrum and on the retention times (GC–MS and GC–FID).

Electrolysis of a solution of 1,4-bis(methylene)cyclohexane (2) in acetonitrile

A solution of tetraethylammonium perchlorate (TEAP) (4.6 g, 0.1 M) in 200 ml acetonitrile was degassed for 30 min by nitrogen ebullition. 1,4-Bis(methylene)cyclohexane (**2**) ($2.5 \text{ g}, 2.3 \times 10^{-2}$ mol) was then added to the solution and the mixture was electrolysed ($\Delta V = 2.55 \text{ V}$) for 21 days. A total of 1728 C were consumed during this period. The solvent was evaporated and the residue was chromatographed on silica gel (MPLC) using a hexanes–diethyl ether gradient. The products and some mixtures were further purified by DCFC using hexanes or a hexanes–(5% diethyl ether–95% hexanes) gradient. Compound **40** was further purified by preparative GC.

1,4-Dimethylbenzene (39). **39** was identified on the basis of its mass spectrum: m/z 106 (M^+ , 57%), 105 (29), 103 (8), 91 (100), 79 (11), 78 (10), 77 (19), 65 (10), 63 (9), 53 (5), 52 (7) and 51 (18);

retention time (GC–FID and GC–MS) and mass spectrum compared to that of an authentic sample (Aldrich).

4-Methylbenzaldehyde (40). $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 9.97 (s, 1H), 8.00 (d, 7.94, 2H), 7.28 (d, 7.93, 2H), 2.44 (s, 3H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 192.03 (d), 145.55 (s), 134.16 (s), 129.85 (d), 129.70 (d) and 21.88 (q); m/z 120 (M^+ , 77%), 119 (94), 91 (100), 89 (12), 74 (3), 65 (40), 64 (5), 63 (24), 62 (11) and 51 (16); retention time (GC–FID and GC–MS), mass spectrum and ^1H and ^{13}C NMR spectra were compared to those of the pure compound (Aldrich).

N-(4-Methylbenzyl)acetamide (41). **41** was recrystallized from cyclohexane; mp 107–108 °C (lit.³¹ 111–112 °C); $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3291 (s), 3076 (w), 2923 (m), 2854 (w), 1646 (s), 1635 (s), 1553 (s), 1518 (m), 1463 (w), 1436 (w), 1374 (w), 1356 (w), 1290 (w), 1279 (w), 1094 (w), 1024 (w), 806 (w) and 731 (w); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 7.20–7.12 (m, 8.55, 4H), 5.77 (br s, 1H), 4.38 (d, 5.49, 2H), 2.34 (s, 3H) and 2.01 (s, 3H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 169.80 (s), 137.26 (s), 135.14 (s), 129.35 (d), 127.86 (d), 43.50 (t), 23.28 (q) and 21.07 (q); m/z 163 (M^+ , 62%), 148 (11), 120 (45), 106 (100), 105 (34), 91 (23), 77 (22) and 65 (13) (M^+ , 163.1000). $\text{C}_{10}\text{H}_{13}\text{NO}$ requires M , 163.0997).

N-(1-Methyl-4-methylenecyclohexyl)acetamide (42). Mp 94–95 °C; $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3316 (s), 3077 (w), 2966 (m), 2934 (m), 2852 (w), 1647 (s), 1553 (s), 1442 (m), 1371 (m), 1323 (w), 1299 (w), 1271 (w), 1132 (w), 951 (w) and 885 (w); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 5.22 (br s, 1H), 4.64 (s, 2H), 2.16 (t, 4.88, 2H), 2.14 (s, 2H), 2.08 (t, 4.27, 2H), 1.96 (s, 3H), 1.57–1.45 (m, 2H) and 1.40 (s, 3H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 169.70 (s), 147.47 (s), 107.73 (t), 53.09 (s), 37.71 (t), 30.40 (t), 25.67 (q) and 24.61 (q); m/z 167 (M^+ , 8%), 110 (29), 108 (87), 93 (100), 91 (20), 79 (27), 70 (18) and 60 (63) (M^+ , 167.1295). $\text{C}_{10}\text{H}_{17}\text{NO}$ requires M , 167.1310).

N-(1,4-Dimethylcyclohex-3-enyl)acetamide (43). $\nu(\text{CDCl}_3)/\text{cm}^{-1}$ 3303 (s), 3077 (w), 2964 (m), 2923 (s), 2852 (w), 1650 (s), 1551 (s), 1442 (m), 1372 (m), 1301 (w) and 1277 (w); $\delta_{\text{H}}(\text{CDCl}_3, \text{AC250})$ 5.24 (br s, 1H), 2.31 (dt, 5.49, 1H), 2.13 (s, 2H), 1.92 (s, 5H, $\text{CH}_3 + \text{CH}_2$), 1.66 (s, 3H), 1.51 (dt, 7.33, 1H) and 1.41 (s, 3H); $\delta_{\text{C}}(\text{CDCl}_3, \text{AC250})$ 169.86 (s), 134.26 (s), 117.62 (d), 51.52 (s), 38.59 (t), 31.49 (t), 27.55 (t), 25.07 (q), 24.49 (q) and 23.26 (q); m/z 108 (96%), 99 (7), 93 (100), 91 (22), 77 (15), 60 (24) and 57 (68) (M^+ , 167.1287). $\text{C}_{10}\text{H}_{17}\text{NO}$ requires M , 167.1310).

Acid-catalysed reaction of 1,4-bis(methylene)cyclohexane (2) in acetonitrile

Concentrated sulfuric acid (0.20 g, 1.8×10^{-3} mol) was added dropwise to a solution of 1,4-bis(methylene)cyclohexane (**2**) (0.18 g, 1.9×10^{-3} mol) in acetonitrile (15 ml). The mixture was stirred for 14 h. Analysis of the product mixture by GC–MS and GC–FID showed that three products (**39**, **42** and **43**) were formed in a ratio of 10:5:1 (GC–FID). This ratio changed to 48:22:1 after 24 h. The identification of the products was based on their mass spectra and their retention times (GC–MS and GC–FID).

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