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Electron transfer induced dissociations of 2- and 4-alkyl cyclohexadienones

Andrew J. McCarroll,[†] Joe A. Crayston and John C. Walton*

School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife KY16 9ST, UK

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Abstract—Several 2- and 4-alkylcyclohexadienones were prepared and shown to accept electrons to produce ketyl radical anions that dissociated rapidly at room temperature to release carbon-centered radicals and an aromatic phenoxide type anion. In the PET process with benzyl-substituted cyclohexadienones, initiated with triethylamine, the benzyl radicals dimerised or abstracted an H-atom from solvent. In electrochemical reductions, and in reductions with alkali metals in liquid ammonia, the benzyl radicals were further reduced to anions.

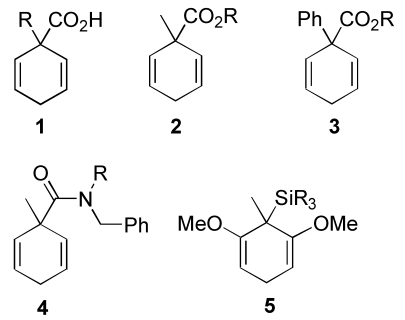
1. Introduction

Cyclohexadiene derivatives **1**–**4** have been successfully employed as precursors in ring-forming free-radical processes,[1–4] as have silylated cyclohexadienes e.g. **5** (Scheme 1).[5]

The driving force for radical production from these 'pro-aromatic' compounds was the restoration of aromatic character on release of a C- or Si-centered radical from the initial cyclohexadienyl radical.

These findings sparked the idea that single electron transfer (SET) to a suitably substituted cyclohexadienone **6** could produce a delocalised ketyl type radical **7** that should easily dissociate in an analogous way.

Release of a C-centered radical R˙ would be favoured because of restoration of aromaticity in the phenolate co-product **8** (Scheme 2). Potentially this could constitute a clean, organotin-free, method of generating various functionalised radicals that could subsequently cyclize or take part in cascade processes. Tanko and co-workers[6] have provided a precedent in their work with 1,1-dimethyl-5,7-di-*t*-butyl-spiro[2.5]octa-4,7-diene-6-one **9**. This reagent accepted an electron from nucleophiles to afford ketyl anion radical **10** that underwent the intramolecular version of the dissociation to produce radical anion **11** (Scheme 3).



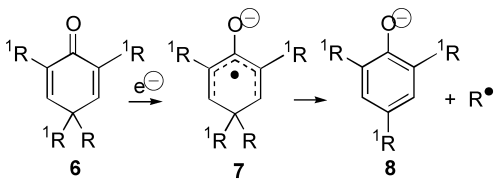
Scheme 1. Cyclohexadiene-based reagents for radical production.

Radical coupling then led to apparent nucleophilic substitution at the more-hindered carbon.

We report here our study of the preparation of model 2- and 4-substituted cyclohexadienones and their subsequent behaviour on accepting electrons under several different sets of experimental conditions.

2. Results and discussion

Reports of preparations of 4,4-dialkylcyclohexa-2,5-dienones are comparatively rare. Schmid and co-workers



Scheme 2. Proposed radical release from cyclohexadienones.

Keywords: free radicals; electron transfer; cyclohexadienones; Birch reductions.

* Corresponding author. Tel.: +44-1334-463864; fax: +44-1334-463808; e-mail: jcw@st-and.ac.uk

† Present address: Cancer Research Laboratories, The Pharmacy School, University of Nottingham, University Park, Nottingham NG7 2RD, UK.

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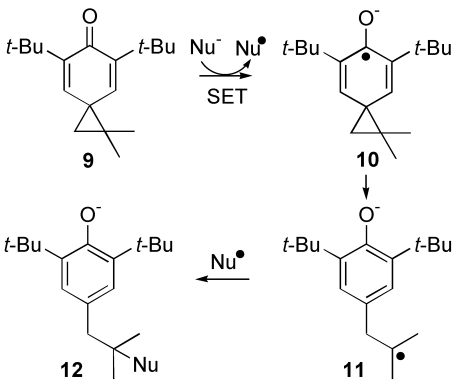
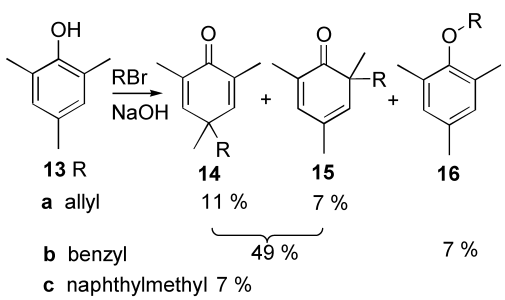


Scheme 3. SET reaction of 1,1-dimethyl-5,7-di-*t*-butylspiro[2.5] octa-4-7-dien-6-one.

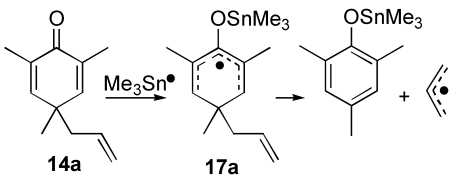
alkylated phenols with alkyl halides in the presence of NaOH.[7] Miller and Margulies found that KOBu-*t* in *t*-BuOH gave higher yields of *C*-alkylated products than NaH in DMSO, which tended to favour formation of *O*-alkylated products.[8] Initially we focussed on alkylating 2,6-di-*t*-butyl-4-methylphenol (BHT). However, this compound was not sufficiently soluble in NaOH for the Schmid method (see Section 4.1.4).[9]

We next chose methyl substituted phenols and focussed on 2,4,6-trimethylphenol (mesitol, **13**) because methyl is the least stabilised of the simple alkyl radicals. It follows that the unwanted β-scission of the intermediate **7** (^{1}R=Me) to produce a methyl radical and a phenol, instead of the desired radical R$^{\cdot}$, should be strongly disfavoured. We carried out alkylations of mesitol with several organo-halides and obtained in each case mixtures of the 2- and 4-alkylated products (Scheme 4). A major cause of the low isolated yields recorded in Scheme 4 was the difficulty in separating pure **14** from **15** by chromatography. Much higher yields of mixtures of **14** and **15** could have been obtained. The 2-alkyl-isomers **15** are expected to accept electrons and yield isomeric delocalised ketyl radicals, that should also release alkyl radicals in a similar way. It was anticipated, therefore, that **14/15** mixtures could be used in preparative work without the need for separation.

The viability of the dissociation was first examined by reactions of each of **14** and **15** using EPR spectroscopy to monitor radical production. Solutions of **14a** with triethylamine as photoelectron transfer (PET) agent showed no EPR spectra. However, when a solution of **14a** (or **15a**) and $Me_3SnSnMe_3$ in *t*-butylbenzene was photolysed in the resonant cavity of the EPR spectrometer, the spectrum of the



Scheme 4. Alkylation of mesitol.



Scheme 5. Tin radical-mediated production of allyl radicals.

allyl radical (a(1H)=4.2, a(2H)=13.9, a(2H)=14.8 G at 270 K), with parameters identical to those given in the literature,[10] was observed at temperatures above 230 K. The photochemically produced trimethyltin radicals added to the carbonyl oxygen giving radical **17** that dissociated even at temperatures as low as 230 K to release the allyl radical (Scheme 5).

At lower temperatures, broad signals were observed that may have corresponded to radical **17a** but definite identification was not possible. EPR experiments with **14b** and **14c** did not show any identifiable radicals.

In order to develop preparative methodology, free of organotin compounds, PET using triethylamine was next examined by product analysis. Photolysis of a solution of **15b** and 10 equiv. of Et_3N in THF by a 400 W medium pressure Hg lamp for 4 h at ambient temperature led to formation of toluene and mesitol as the major products. The analogous PET reaction of **14b** was examined in acetonitrile (ACN). This is a much poorer H-donor than THF and hence the benzyl radicals preferentially coupled to give bibenzyl in this solvent. Table 1 shows yields from a reaction of **14b** and Et_3N in ACN. These PET reactions demonstrated the ability of **14b** and **15b** to generate benzyl radicals, however, it was difficult to obtain complete conversion of the substrate (Table 1). Furthermore, excess Et_3N had to be used and GC–MS analyses revealed several additional products formed by abstraction of an H-atom from Et_3N to give $Et_2NCH^{\cdot}CH_3$ radicals that subsequently coupled with the cyclohexadienyl **7**, and other radicals in the system.

Cyclic voltammograms were obtained for solutions of **14b** and **15b** in ACN (ca. 10^{-3} M) with $TBAPF_6$ as supporting electrolyte. The two dienones showed irreversible reduction waves with E_p^c at −2.42 and −2.26 V vs ferrocene, respectively [i.e. E_p^c=−1.77 and −1.61 V vs SHE]. Interestingly, simulation of the responses showed these

Table 1. Products from reductions of benzyltrimethyl-cyclohexadienones

Dienone	Method	PhMe[a] (%)	Bibenzyl (%)	Mesitol **13** (%)	Other (%)
14b	Et_3N/ACN/$h\nu$	0	45	31	**14b** (24)[b]
14b	Electrochemical	[12]	0	29	[c]
15b	Electrochemical	[10]	0	12	[c]
14b	Na/NH_3	[8]	0	84	
15b	Na/NH_3	[21]	0	51	[d]
14b	Li/NH_3	[1]	2	73	**14b** (5)[b,d]

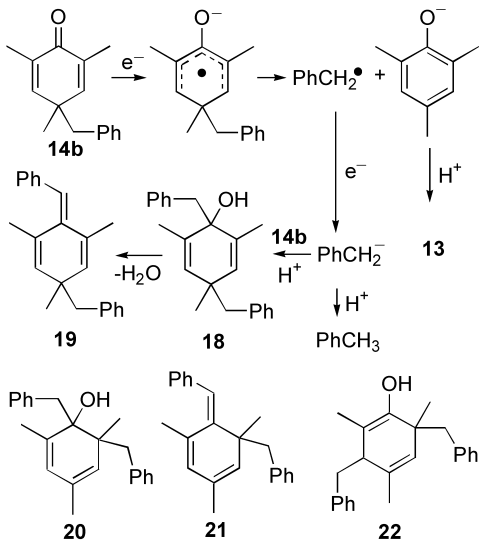
[a] Toluene yields were seriously depressed because of loss during solvent/NH_3 evaporation.
[b] Unreacted substrate.
[c] Unreacted substrate present.
[d] Products from benzyl anion addition observed.

were two-electron waves in both cases, suggesting that formation of the ketyl radical anion **7** was followed by release of the benzyl radical and its immediate reduction to the benzyl anion (an ECE reaction). The scan-rate dependence of this reduction appeared to show that **15b** released the benzyl group in the chemical step approximately one order or magnitude more slowly than **14b**.

Preparative reductions of **14b** and **15b** were carried out by electrolysing ca. 10^{-3} M solutions of the substrates [$TBAPF_6$ (0.1 M) as supporting electrolyte] with a rotating glassy carbon electrode for 4–5 h at 22°C. Complete separation of the products from the excess $TBAPF_6$ was not achieved, but product analysis by ^1H NMR and GC–MS showed the production of toluene and mesitol in both cases (Table 1). Yields were modest and this was partly due to the presence of much unreacted starting material and partly to contamination with Bu_3N from the electrolyte.

The observed reduction potentials suggested[11] that sodium in liquid ammonia ($E'^0=-2.25$) or lithium in liquid ammonia ($E'^0=-2.64$ V) would be suitable for preparative work. Reaction of **14b** with Na/NH_3 gave a very clean reaction in which mesitol and toluene were virtually the only products (Table 1). The reaction of **14b** with Li/NH_3 was also comparatively clean, but minor amounts of dibenzylated compounds accompanied the mesitol and toluene. The GC/MS of the products from the reaction of **14b** with Li/NH_3 showed a significant deoxygenated product [$M^+=300$, probably $C_{23}H_{24}$] that most likely had structure **19**. This could have formed by nucleophilic addition of the benzyl anion to the carbonyl oxygen atom of **14b**, followed by dehydration (Scheme 6) and hence this provides independent evidence of the intermediacy of the benzyl anion in these Birch type reductions.

The yield of mesitol **13** was lower for the reaction of the 2-benzyl compound **15b** with Na/NH_3 and, in addition to toluene, the GC–MS chromatogram showed a small amount of a compound having $M^+=320$ and another having $M^+=300$. These products probably had structures **20** and **21**, respectively, from nucleophilic addition of the benzyl anion to the reactant (Scheme 6). Obviously, isomeric structures such as **22** (or its keto tautomer, formed by Michael type addition) for the product with $M^+=320$, cannot be ruled out. However, dehydration (which may have occurred during work-up) would be easier from structure **20** hence detection of **21** (and **19**) suggests that the majority of nucleophilic addition occurred at the carbonyl carbon-atom of the substrate. Traces of a product having $M^+=210$ (probably $C_{16}H_{18}$, i.e. 1-benzyl-2,4,6-trimethylbenzene) were also detected in these reductions. This could have been formed by loss of benzyl alcohol, instead of water, from **18** and **20**. In all these reactions, the yield of toluene was artificially low because it escaped during NH_3 and/or solvent evaporation.



Scheme 6. Reduction of benzyltrimethylcyclohexadienones.

3. Conclusion

These reactions showed that cyclohexadienones trap electrons well under a range of conditions, and that the ketyl radical anions dissociate rapidly and efficiently to generate the corresponding phenol and release a C-centred fragment (Scheme 5). The best conditions for preparative purposes involved sodium and liquid ammonia. The benzyl moiety released in the reactions studied here has a comparatively small reduction potential (ca. −1.2 V vs SHE in ACN)[12] and was immediately reduced to the benzyl anion electrochemically and with alkali metals.

Primary and secondary alkyl radicals, however, have larger reduction potentials (ca. −2.0 V vs SHE)[13] and hence these species should be the main intermediates released in reductions of 2- and 4-*n*-alkylcyclohexadienones using Na/NH_3. Although the reduction potential of the 2-substituted derivative was more negative than that of the 4-substituted derivative, and it released the benzyl radical somewhat more slowly, these differences were not very significant during alkali metal Birch-type reductions. The results indicate that an overall process starting with say, a 5-alkenyl bromide, leading to the corresponding cyclised product should be viable. A mixture of 2- and 4-alkenylcyclohexadienones would be produced in the alkylation step and this, on treatment with Na/NH_3, should give the alk-5-enyl radical that would cyclise to afford the desired product. Only if the cyclised radical had a low reduction potential due to resonance would carbanion formation divert the process away from 5-*exo*-ring closure.

4. Experimental

4.1. General

^1H NMR spectra and ^{13}C NMR were obtained using a Bruker AM 300 MHz spectrometer. All samples were dissolved in deuteriochloroform, unless otherwise stated, using tetramethylsilane as an internal standard. Mass spectra were obtained with 70 eV electron impact ionisation on a VG Autospec spectrometer. GC/MS work was carried out using a Finnegan Incos 50 quadrupole mass spectrometer coupled to a Hewlett–Packard HP5890 capillary gas chromatograph fitted with a column coated with

methylsilicone as the stationary phase or with the VG Autospec coupled to a similar GC. Typically the temperature was programmed from 40 to 250°C at 12°/min and the flow rate was ca. 0.5 mL/min. EPR spectra were recorded with a Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation. Solutions were placed in 4 mm o.d. quartz tubes and illuminated by UV light from a 500 W super pressure mercury lamp focussed directly into the EPR resonant cavity. Cyclic voltammetry was carried out using a PC-controlled EG and PAR 273A potentiostat with an undivided, teflon-topped beaker-type cell (ca. 25 mL) equipped with a glassy carbon working electrode (0.071 cm^2), a silver wire quasi-reference electrode and a platinum wire counter electrode. The number of electrons passed was determined by comparing the current with that of ferrocene which is known to give a one-electron wave, and whose diffusion coefficient is known to be 2×10^{-5} cm^2 s^{-1}. The scan-rate dependence of the data was simulated using the Digisim 3.0 program (Bioanalytical Systems Inc, West Lafayette, Indiana).[14]

4.1.1. 4-Allyl-2,4,6-trimethylcyclohexa-2,5-dienone (14a) and 2-allyl-2,4,6-trimethylcyclohexa-3,5-dienone (15a).[7] To a solution of NaOH (1.6 g; 0.04 mol) in water (20 cm^3) was added mesitol (5.45 g; 0.04 mol), and the mixture was stirred overnight. A further 0.2 g NaOH and 10 cm^3 H_2O was added to obtain complete solution. Allyl bromide (3.85 g; 0.044 mol) was added dropwise, and the mixture was stirred for 24 h at room temperature. The mixture was extracted with pentane (3×50 cm^3), and washed with 10% sodium hydroxide solution (2×50 cm^3) and water (3×50 cm^3), then dried ($MgSO_4$), and concentrated. Purification by column chromatography (pentane/diethyl ether 9/1) yielded 4-allyl-2,4,6-trimethyl-cyclohexa-2,5-dienone **14a** (0.41 g; 11%) and 2-allyl-2,4,6-trimethyl-cyclohexa-3,5-dienone **15a** (0.24 g; 7%), both as colourless oils, with satisfactory NMR and IR spectra.[7]

4-Allyl-2,4,6-trimethylcyclohexa-2,5-dienone (**14a**). ν_{max}/cm^{-1} 1670 (C=O) 994 and 916 (CH=CH_2). δ_H1.19 (3H, s, CH_3 on C-4), 1.89 (6H, s, CH_3 on C-2,6), 2.27 (2H, d, J=7.4 Hz, allyl Hs), 4.98–5.03 (2H, m, =CH_2), 5.51–5.62 (1H, m, -CH=CH_2), 6.66 (2H, s, =CH).

2-Allyl-2,4,6-trimethyl-cyclohexa-3,5-dienone (**15a**). δ_H 1.12 (3H, s, CH_3), 1.84 (3H, s, CH_3), 1.90 (3H, s, CH_3), 2.11–2.59 (2H, m, allyl Hs), (4.85–5.02 (2H, m, CH=CH_2), 5.41–5.63 (1H, m, CH=CH_2), 5.85 (1H, s, =CH), 6.69 (1H, s, =CH).

4.1.2. 2-Benzyl-2,4,6-trimethyl-cyclohexa-3,5-dienone (15b) and 4-benzyl-2,4,6-trimethyl-cyclohexa-2,5-dienone (14b). To solution of NaOH (6.0 g 0.15 mol) in water (100 cm^3) was added mesitol (20.4 g; 0.2 mol) and the mixture was stirred (and sonicated) until most passed into solution. Benzyl bromide (25.6 g; 0.15 mol) was added over a period of 20 min and the mixture was heated at 60°C for 2 h, then allowed to cool (with stirring). The mixture was extracted with pentane (3×100 cm^3) and washed with 10% NaOH solution (2×50 cm^3) then water (4×20 cm^3) and dried ($MgSO_4$) and concentrated. The mixture was separated by column chromatography (pentane/diethyl ether, 9/1) to afford *O*-benzyl-mesitol (2.4 g, 7%), **14b** (0.9 g, 2.7%) and **15b** (2.5 g, 7.4%).

Compound **14b**. δ_H 1.22 (3H, s), 1.83 (6H, s), 2.79 (2H, s), 6.59 (2H, s) 7.0–7.3 (5H, m); δ_C 16.1 (CH_3), 25.2 (2×CH_3), 41.5 (C), 47.2 (CH_2), 126.6 (CH), 127.8 (CH), 130.1 (CH), 134.1 (C), 136.6.(C), 150.4 (CH), 187.2 (CO); found M^+=226.1366; $C_{16}H_{18}O$ requires 226.1358.

Compound **15b**. δ_H (300 MHz, $CDCl_3$) 1.21 (3H, s, CH_3 at C-4), 1.76 (3H, s, CH_3), 1.82 (3H, s, CH_3), 2.70 (1H, d, J_1=12.8 Hz), 3.08 (1H, d, J=12.8 Hz), 5.87 (1H, s, =CH), 6.46 (1H, s, =CH), 6.99–7.01 (2H, m, ArH), 7.13–7.20 (3H, m, ArH); δ_C 15.3, 21.1, 24.8, 47.1, 126.3, 127.5, 129.7, 138.7, 142.4, 205.5; found M^+=226.1360, $C_{16}H_{18}O$ requires 226.1358. A mixture of the two isomers was also obtained (13.2 g, 38.9%).

4.1.3. 4-(2-Methylnaphthalene)-2,4,6-trimethylcyclohexa-2,5-dienone (14c). Prepared from 2-(bromomethyl)-naphthalene and **13** as described above yielding, after column chromatography, **14c** (0.10 g; 7%), together with much unreacted starting material. The product contained some 2-(bromomethyl)naphthalene as an impurity which was not removed by recrystallisation. δ_H 2.15 (3H, s, CH_3), 2.19 (3H, s, CH_3), 2.24 (3H, s, CH_3), 4.18 (2H, s, CH_2), 6.90 (2H, s, =CH), 7.2–7.8 (7H, m, ArH). δ_C 12.2, 15.9, 19.7, 35.5, 127.8, 128.8, 129.7, 131.9, 133.6, 135.3, 137.5, 150.3. (Found M^+ 276.1512; $C_{20}H_{20}O$ requires M 276.1514).

4.1.4. 2,6-Di-*t*-butyl-4-hexadecyl-4-methylcyclohexa-2,5-dienone. To 2,6-di-*t*-butyl-4-methylphenol (4.41 g; 0.02 mol) in dry THF (30 cm^3) in a nitrogen atmosphere was added potassium *t*-butoxide, followed by further THF (20 cm^3). The mixture was stirred for 1 h (in which time the mixture went a peach colour) the iodohexadecane (7.05 g; 0.02 mol) was added, and the mixture stirred for 24 h, refluxed for 6 h, then stirred for 5 days. Water (40 cm^3) and ether (40 cm^3) were added, and the organic layer separated, then washed with water, brine, and water again. The organic layer was dried ($MgSO_4$), then purified by column chromatography (PE/EtOAc). The fastest running spot was isolated (impure) and again purified by column chromatography (pentane/ether 9/1). A very small amount (0.07 g; 0.8%) of 2,6-di-t-butyl-4-hexadecyl-4-methylcyclohexa-2,5-dienone was isolated as a yellow oil. δ_H 0.88 (3H, t, J=6.6 Hz, CH_3). 1.12–1.28 (39H, m), 6.40 (2H, s, =CH) δ_C 14.1, 22.7, 24.7, 27.1, 29.1, 29.2, 29.4–29.7, 29.9, 30.3, 30.4, 31.9, 34.6, 40.0, 41.4, 146.3, 147.0, 186.7. (Found M^+ 444.4337. $C_{31}H_{56}O$ requires M 444.4331).

4.1.5. Photoinitiated reaction of 2-benzyl-2,4,6-trimethylcyclohexa-3,5-dienone with triethylamine. Dienone **15b** (0.09 g), and triethylamine (0.1 g; 5 equiv.) were dissolved in acetonitrile (1 cm^3). The mixture was degassed with nitrogen, and illuminated using a 400 W mercury lamp for 4 h. The products were analysed using GC/MS; peak no. 125, toluene (trace); peak no. 294, 2,4,6-trimethylphenol, and peak no. 410, bibenzyl, together with several unidentified components.

4.1.6. Photoinitiated reaction of 4-benzyl-2,4,6-trimethylcyclohexa-2,5-dienone with triethylamine. The dienone **14b** (0.021 g, 0.09 mmol) and triethylamine (0.022 g, 0.22 mmol) were dissolved in C_6D_6 (0.5 cm^3) in a quartz tube and irradiated with light from a 400 W

medium pressure Hg lamp for 4 h at ambient temperature. ^{1}H NMR analysis showed Et_3N, unreacted **14b** (24%), 2,4,6-trimethylphenol (**13**) (31%) and bibenzyl (2.9 ppm, s) (45%) together with unresolved signals from other products. GC–MS analysis showed the following components (in order of elution) peak 249, 2,4,6-trimethylphenol, peak 260, 2,4,6-trimethylcyclohexa-2,5-dienone or 2,4,6-trimethylcyclohexa-2,4-dienone, peak 362 bibenzyl *m/z* (%) 182 (M^+, 22), 92 (8), 91 (100), 65 (12) (library fit 987), peaks 436 and 444, 4-(1-diethylamino-ethyl)-2,4,6-trimethyl-cyclohexa-2,5-dienone and 2-(1-diethylamino-ethyl)-2,4,6-trimethyl-cyclohexa-2,5-dienone *m/z* (%) 233 (M^+, 13), 211 (25), 210 (87), 196 (30), 195 (100), 180 (25), 165 (22), 132 (20), 119 (22), 100 (20) together with unreacted starting materials and several unidentified compounds. The above photolysis was repeated but with THF (0.5 cm^3) as solvent. GC–MS analysis showed toluene and 2,4,6-trimethylphenol as the main products.

4.1.7. Reduction of 4-benzyl-2,4,6-trimethylcyclohexa-3,5-dienone with Li in ammonia. To the dienone **14b** (0.21 g, 0.9 mmol) in liquid ammonia (30 cm^3) was added Li metal (20 mg, 2.9 mmol) in small pieces. The solution was stirred for 1.5 h, then quenched with NH_4Cl (0.5 g) and the ammonia evaporated. The residue was extracted with diethyl ether, dried ($MgSO_4$) evaporated and dissolved in $CDCl_3$. The ^{1}H NMR spectrum showed unreacted dienone (5%), mesitol (73%), toluene (1%), bibenzyl (2%) and several minor unidentified components. GC–MS: peak 59; toluene, peak 290; mesitol, peak 366; dibenzyl, peak 431; probably 1-benzyl-2,4,6-trimethylbenzene *m/z* (%) 210 (M^+, 72), 195 (100), 196 (13), 180 (14), 179 (11), 178 (9), 165 (15), 133 (12), 132 (16), 91 (14), peak 447; unreacted **14b**, peak 602; *m/z* (%) 300 (M^+, 2), 210 (18), 209 (100), 194 (9), 193 (6), 179 (18), 176 (9), 165 (5), 91 (13), probably $C_{23}H_{24}$, 1-phenylmethylene-2,4,6-trimethyl-4-benzylcyclohexa-2,5-diene, peak 655; *m/z* (%) 301 ($M+1^+$, 23), 300 (M^+ 100), 285 (10), 210 (11), 209 (82), 207 (13), 194 (12), 193 (14), 192 (13), 179 (21), 91 (28); probably $C_{23}H_{24}$, 1,3-dibenzyl-2,4,6-trimethylbenzene.

4.1.8. Reduction of 4-benzyl-2,4,6-trimethylcyclohexa-3,5-dienone with Na in ammonia. To the dienone **14b** (0.1 g, 0.44 mmol) in liquid ammonia (20 cm^3) was added Na metal (25 mg, 1.1 mmol) in small pieces. The solution was stirred for 1 h, then quenched with NH_4Cl (0.1 g) and the ammonia evaporated. The residue was extracted with $CDCl_3$ dried ($MgSO_4$) and filtered. The ^{1}H NMR spectrum showed essentially only mesitol (84%) and toluene (8%). The GC–MS confirmed this showing toluene, and mesitol together with only traces of the compounds having MS data the same as peaks 431, 602 and 655 from above.

4.1.9. Reduction of 2-benzyl-2,4,6-trimethylcyclohexa-3,5-dienone 15b with Na in ammonia. To dienone **15b** (0.2 g, 0.88 mmol) in liquid ammonia (25 cm^3) was added Na metal (50 mg, 2.2 mmol) in small pieces. The solution was stirred for 1 h, then quenched with NH_4Cl (0.1 g) and the ammonia evaporated. The residue was extracted with $CDCl_3$ dried ($MgSO_4$) and filtered. The ^{1}H NMR spectrum showed unreacted **15b**, mesitol (51%) and toluene (21%) together with several minor, poorly resolved resonances. The GC–MS showed toluene, mesitol, and unreacted **15b** together with a trace of 1-benzyl-2,4,6-trimethylbenzene (MS as above), peak 623, *m/z* (%) 320 (M^+, 4), 319 (9), 318 (5), 229 (5), 228 (15), 227 (10), 200 (5), 105 (5), 92 (9), 91 (100), 65 (6), probably $C_{23}H_{26}O$, peak 639 (minor) *m/z* (%) 301 (M+1, 10), 300 (M^+, 38), 285 (5), 230 (14), 229 (58), 209 (30), 179 (8), 137 (23), 123 (12), 91 (100), 43 (13), probably $C_{23}H_{24}$, plus several minor unidentified components.

4.2. Electrochemistry

4.2.1. Cyclic voltammetry of 14b and 15b. The cyclic voltammograms (CVs) for **14b** and **15b** were obtained as described above. Compound **15b** was reduced at a more positive potential (ca. 150 mV) than **14b**. The reduction current was that expected for a two-electron reduction based on a comparison with a ferrocene wave of known concentration. There was a smaller wave at more cathodic potentials, at about −3.2 V vs Fc/Fc$^+$, just before the solvent breakdown. This could be due to an impurity or to product reduction. On the return scan broad anodic peaks, possibly due to adsorbed products of the main reduction, appeared at about −0.9 and −0.6 V. Using high scan rates and lower temperatures (−40°C) it was not possible to obtain reversible reductions for the main cathodic peaks. However, the scan-rate dependence of the normalized peak currents revealed that the currents due to the peak of **15b** approached that of a one-electron wave at higher scan rates. This behaviour is typical of an ECE (successive steps of Electron transfer/Chemical reaction/Electron transfer) reaction scheme.[15]

$$\mathbf{15b} + e^- \rightarrow \mathbf{15b}^{-\cdot}, \qquad E = -2.26\ \text{V}$$

$$\mathbf{15b}^{-\cdot} \rightarrow \text{PhCH}_{2\cdot} + \text{products}$$

C, unimolecular rate constant k

$$\text{PhCH}_{2\cdot} + e^- \rightarrow \text{PhCH}_2^-, \qquad E \geq -2.26\ \text{V}$$

The data could be modelled using the Digisim program with rate constants for the chemical step of k=5000 and 500 s^{-1} for **14b** and **15b**, respectively. However, it was difficult to obtain precise values for this scheme due to the insensitivity of the data to the parameters and the absence of a reversible potential for the reduction, and so the errors on these rate constants are at least 20%.

4.2.2. Electrochemical reduction of 2-benzyl-2,4,6-trimethylcyclohexa-3,5-dienone 15b. The dienone (7.2 cm^3 of a 4.9 mmol soln) in ACN with $TBAPF_6$ (Fluka, puriss, 0.1 M) as supporting electrolyte was electrolysed at −2.0 V for 5 h at room temperature. A total of 55 C was passed. The ACN was evaporated and the residue taken up in C_6D_6 and filtered to remove $TBAPF_6$. The ^{1}H NMR spectrum of the mixture showed mesitol (12%) and toluene (10%) as well as unreacted starting dienone and residual $TBAPF_6$.

4.2.3. Electrochemical reduction of 4-benzyl-2,4,6-trimethylcyclohexa-3,5-dienone 14b. The dienone (6.1 cm^3 of a 4.9 mmol soln.) in ACN with $TBAPF_6$ (0.1 M) as supporting electrolyte was electrolysed at −2.0 V for 4 h at room temperature (22°C). The ACN was evaporated and the residue taken up in $CDCl_3$ and filtered to remove $TBAPF_6$.

The ^{1}H NMR spectrum of the mixture showed mesitol (29%) and toluene (12%) as well as unreacted starting dienone and residual $TBAPF_6$.

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