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Reactivity and selectivity of aryloxylium ions

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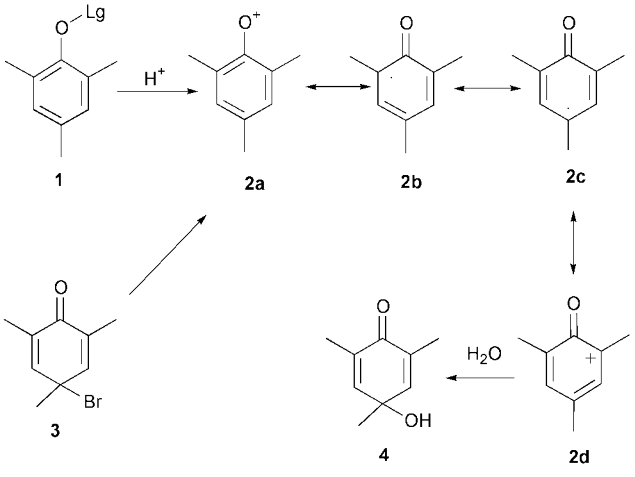
The reactivity and selectivity of aryloxylium ions in acetonitrile–water mixtures are described. The 4-bromo-2,4,6-trialkylcyclohexa-2,5-dienones used as substrates were synthesised by electrophilic bromination in yields of 60% (**3** R = Me) and 52% (**7** R = Bu^t). Under solvolysis conditions **3** and **7** decompose cleanly *via* their respective aryloxylium cations to the 4-hydroxy-2,4,6-trialkylcyclohexa-2,5-dienones **4** and **12**. As the polarity of the solvent increases, the observed rates of reaction increase by a factor of 36 (**3**) and 56 (**7**). A detailed study gave Grunwald–Winstein m_s values of 0.56 (**3**) and 0.63 (**7**). Addition of sodium bromide caused a common ion rate depression with $a = 22.1$ (**3**) and $a = 33.3$ (**7**). Competitive azide trapping gave $k_{az} : k_{MeOH} = 3610$ and $k_{MeOH} : k_{H_2O} = 0.755$, while the lifetime of the cation **11** in water was estimated to be 0.55 µs. Sterically hindered alcohols (propan-2-ol, cyclohexanol) do not trap the aryloxylium ions, instead products of reduction (the corresponding phenols) were formed in quantitative yield. Following a careful search it was determined that these products did not arise from hydride transfer from these alcohols.

Introduction

Aryloxylium ions are six electron cationic species that are isoelectronic with carbenium and nitrenium ions. While the reactivity and selectivity of arylnitrenium ions[1] have been well studied and in particular their carcinogenic activity,[2] the chemistry of aryloxylium ions is less well understood. Aryloxylium ions are intermediates in a number of reactions such as phenolic oxidations as shown by Pelter and co-workers[3] and they have also been implicated in biological processes such as isoflavone synthesis.[4] The positive charge is not stable on the oxygen and can be delocalised on to the *ortho* and *para* positions on the ring[5] (Scheme 1). Thus, nucleophiles generally react at the ring carbons in preference to the oxygen.[3,5] Previous work on these cations has focused on the distribution of products between attack on the oxygen and attack on the ring carbons.[6]

Aryloxylium ions have also been generated by electrochemical[7] and synthetic methods.[5,8] The chemical methods generally involved a leaving group on the oxygen. These leaving groups have included tosylamines[8] and pyridinium tetrafluoroborate[5] in acidic conditions at high temperature. These precursors and conditions are not suitable to study the cations in aqueous acetonitrile at 25 °C. Our method was to approach the cation from a different route by synthesising the 4-bromo-2,4,6-trialkylcyclohexa-2,5-dienone. We now show that this generates the corresponding oxocyclohexadienylium cation in solution (Scheme 1).

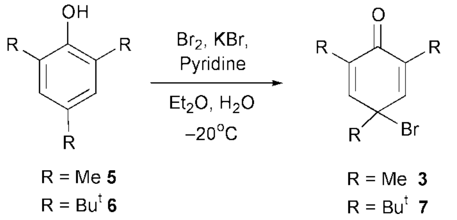


Scheme 1

Results and discussion

Products of reaction

The aryloxylium ion precursors, 4-bromo-2,4,6-trimethylcyclohexa-2,5-dienone **3** (60%) and 4-bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone **7** (52%) were synthesised in good yield *via* an electrophilic bromination of the starting phenols[9] (Scheme 2).



Scheme 2

The bromide **3** was very unstable, decomposing to 3-bromomesitol (3-bromo-2,4,6-trimethylphenol, **9**) *via* the acid-catalysed dienone–phenol rearrangement[9] in non-aqueous solution and to 4-bromomethyl-2,6-dimethylphenol (**8**) when stored in the solid state.[9] Therefore it was important to establish initially the course of the reactions of **3** and **7** under good ionizing conditions using acetonitrile–water mixtures. The possible competing reactions of **3** in solution are shown in Scheme 3.

A repetitive scan from 200 to 350 nm in 80 : 20 acetonitrile–water indicates that the reaction of **3** proceeds cleanly through a tight isosbestic point without a long-lived intermediate. A large scale solvolysis reaction in aqueous acetonitrile indicates the formation of only one solvent trapped product, namely 4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dienone **4**. There was no evidence of the *ortho* trapped product 6-hydroxy-2,4,6-trimethylcyclohexa-2,4-dienone **10**, but there was also some decomposition of precursor **3** to phenol **8** (less than 10%).

The *tert*-butyl-substituted precursor **7** was a significantly more stable precursor than **3**, presumably as a result of the

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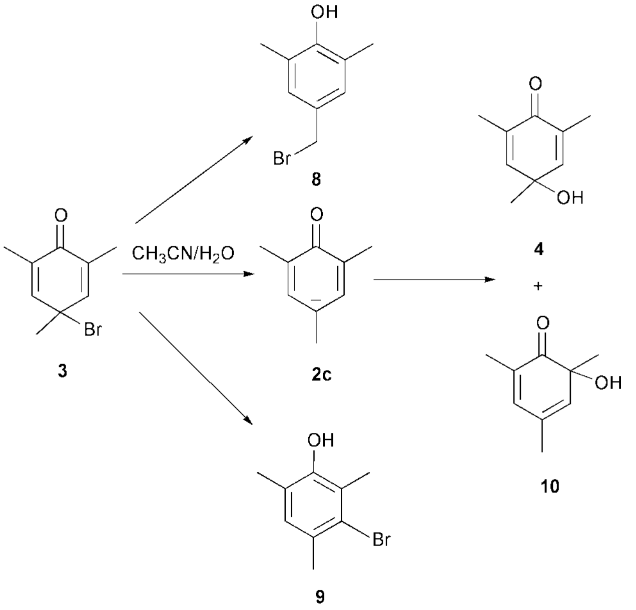
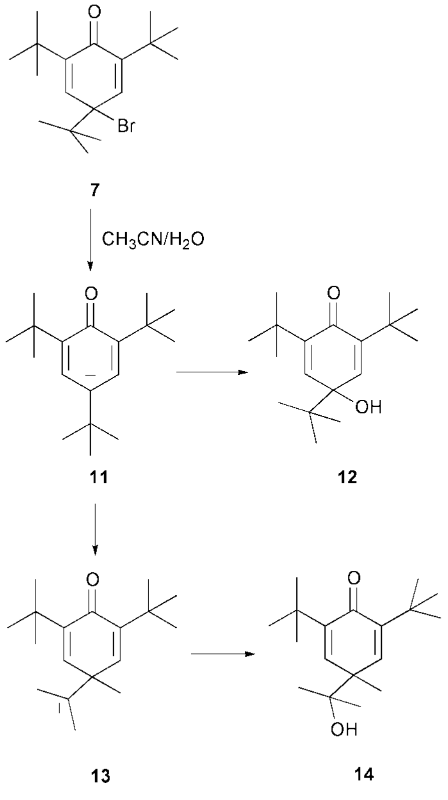


Scheme 3

bulky *tert*-butyl groups blocking the reactive sites. However, in this case we are concerned that in solution the cation **11** might undergo a 1,2-methyl migration to form the more stable tertiary cation (see Scheme 4).



Scheme 4

A repetitive scan of the UV spectrum of **7** from 200 to 350 nm undergoing reaction in 80 : 20 acetonitrile–water again indicates that the reaction proceeds cleanly, with a tight isosbestic point, showing the absence of a long-lived intermediate capable of shifting the isosbestic point. Large scale solvolysis in aqueous acetonitrile yielded 4-hydroxy-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**12**) as the sole product. Again there was no solvent *ortho* trapped product and there was no 1,2-methyl migration to form 4-methylcyclohexa-2,5-dienone **14** under these conditions as shown by ^{1}H NMR analysis. This indicates that there is only one reactive site on the ring. These reactions yield only the cation trapped at the *para* position. The products of the other possible reactions, if present, could have been easily distinguished by ^{1}H NMR analysis of the crude reaction mixture and by the availability of their proton chemical shifts.

Table 1 Observed rate constants for the reaction of **3** and **7** in acetonitrile–water mixtures at 25 °C

% H_2O[a]	**3** k_{obs}/s^{-1}	**7** k_{obs}/s^{-1}
10	3.05×10^{-3}	9.67×10^{-5}
20	1.41×10^{-2}	3.22×10^{-4}
30	2.47×10^{-2}	4.21×10^{-4}
40	5.12×10^{-2}	1.85×10^{-3}
50	1.10×10^{-1}	5.43×10^{-3}

[a] % Water as volume.

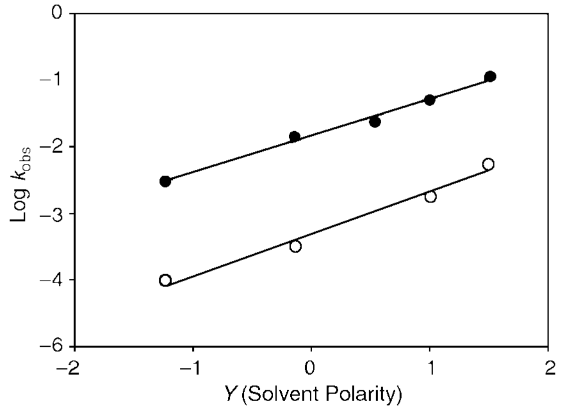


Fig. 1 Grunwald–Winstein plot of log *k vs. Y*.[11] **3** (●) $r = 0.996$ and **7** (○) $r = 0.993$.

Solvent and common ion effects

In order to identify both the reaction mechanism involved in the conversion of **3** to **4** and **7** to **12** and the possible aryloxylium ion intermediates, solvent and common ion effects were examined. The observed pseudo-first-order rate constants (Table 1) were measured at fixed wavelength against time scans at 251 (**3**) and 255 nm (**7**). The observed rate constants increased by a factor of 36 (**3**) and 56 (**7**) as the solvent polarity was increased from 10 to 50% H_2O. This increase was small compared with previously observed values for reactions passing through a compact cationic intermediate. A Grunwald–Winstein plot[10] (Fig. 1) measured the sensitivity of the reaction to solvent polarity giving $m_s = 0.56$ (**3**) and $m_s = 0.64$ (**7**). These values are significantly lower than those observed for simple carbocation formation. For example, the *tert*-butyl cation has an m_s value of 1.00[10] and reactions proceeding through tertiary cationic intermediates usually have m_s values of between 0.8 and 1.2.

The presence of an intermediate aryloxylium ion formed in an S_N1 reaction was unambiguously established however by the observation of a common ion effect (Fig. 2). Addition of sodium bromide resulted in a measurable rate depression in 80 : 20 acetonitrile–water at constant ionic strength ($\mu = 0.10$ M). The slope of the lines in Fig. 2 ($1/k_{obs}$ *vs.* [NaBr]) gives the mass law constants $a = 22.1$ (**3**) and $a = 33.3$ (**7**) respectively. The rate constant for ionisation in the absence of added bromide was calculated from the intercept of the plot as $k_{ion} = 1.19 \times 10^{-2}\ s^{-1}$ for **3** and $k_{ion} = 4.25 \times 10^{-4}\ s^{-1}$ for **7** in 80% acetonitrile–20% water. The mass law constants for **3** and **7** show that the selectivities of the cations **2** and **11** are similar. The *tert*-butyl group does not increase the intrinsic stability and therefore the selectivity of the cation **11** greatly, but it does slow

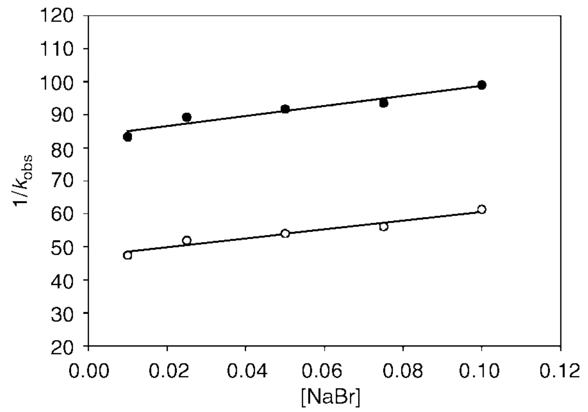


Fig. 2 Common ion effect $1/k_{obs}$ *vs.* [NaBr] in 80% acetonitrile and 20% water for **1** (●) $r = 0.964$ and **7** (○) $r = 0.977$. $1/k_{obs}$ for **7** divided by 50 for ease of presentation.

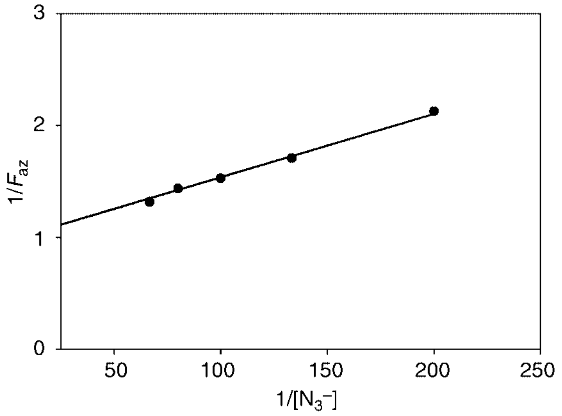


Fig. 3 Azide trap ($1/F_{az}$ *vs.* $1/[NaN_3]$) for **7**. Solvent 50 : 50 acetonitrile–MeOH. Ionic strength was maintained at 0.015 M with $NaClO_4$ ($r = 0.995$). Product ratios were calculated from ^1H proton NMR analysis.

down the initial ionisation step, possibly due to the prevention of solvent assistance by steric hindrance. These results parallel those of Richard and co-workers who have shown that rates of formation of α-substituted 4-methoxybenzyl cations vary considerably but that the lifetime and trapping of the cations are relatively unaffected by structure.[12]

Azide trap and lifetimes

The azide trap was used to calculate the ratio of azide attack to solvolysis by methanol (Fig. 3) of **7** in 50 : 50 acetonitrile–methanol mixtures ($\mu = 0.015$ M). The product ratios were determined by the ratio of integration for the vinylic hydrogens at 6.59 (azide **16**) and 6.54 ppm (methoxy **17**). The fraction of azide product was determined according to eqn. (1) and the results were fitted to eqn. (2).

$$F_{az} = f_{az}/(f_{MeOH} + f_{az}) \qquad (1)$$

$$f = \text{integral of peak}$$

$$1/F_{az} = 1.00 + k_{MeOH}[H_2O]/k_{az}[NaN_3] \qquad (2)$$

Because the azide **16** and the hydroxy product **12** have similar ^1H NMR spectra, the possibility of a product resulting from water attack contributing to the product ratio was precluded by careful IR and ^{13}C NMR analysis. The characteristic hydroxy peak at 3482 cm^{-1} in the infra-red spectra was absent in the isolated crude mixture. Again from analysis of the ^1H NMR there was only attack at the *para* carbon with no evidence for any attack at the *ortho* positions.

From the slope of the line in Fig. 3 the $k_{az} : k_{MeOH}$ ratio was calculated to be 3610 M^{-1}. Assuming that azide attack is diffusion controlled ($k_{az} = 5 \times 10^9$ s^{-1} M^{-1}) then the absolute value of $k_{MeOH} = 1.4 \times 10^6$ s^{-1}. From competition studies with a solvent consisting of 80% acetonitrile, 10% MeOH and 10% H_2O, the ratio of $k_{MeOH} : k_{H_2O}$ was calculated by determining the ratio of integration of vinylic peaks at 6.59 ppm **12** and 6.54 ppm **17**. The $k_{MeOH} : k_{H_2O}$ ratio was calculated to be 0.755 [eqn. (3)].

$$k_{MeOH}/k_{H_2O} = ([\mathbf{17}]/[\mathbf{12}])([H_2O]/[MeOH]) \qquad (3)$$

This is unexpected since MeOH is generally a superior nucleophile for cations than is water. We attribute this inverse result to the steric bulk of the *tert*-butyl groups, which preferentially slows the methanol attack.

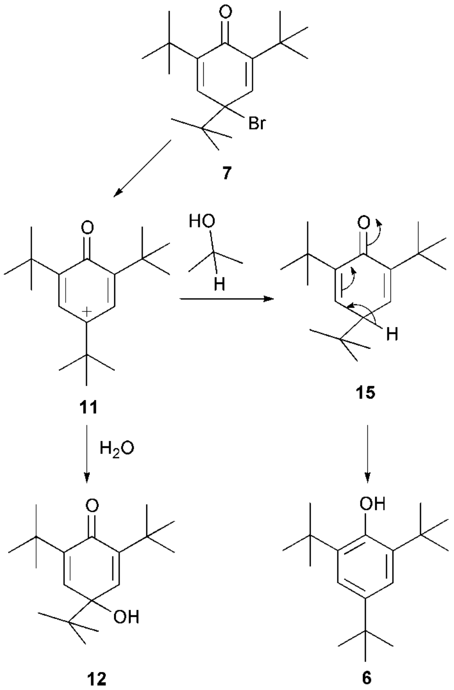
When the *tert*-butyl groups were replaced with methyl groups the $k_{MeOH} : k_{H_2O}$ ratio for the trapping of **2** was found to be 1.56. This shows the reduced steric hindrance of the methyl group in this cation relative to the *tert*-butyl groups resulting in the expected rates of methanol attack relative to water attack. The $k_{MeOH} : k_{H_2O}$ ratio is however low when compared with the 4-methylbenzyl cation that has a $k_{MeOH} : k_{H_2O}$ ratio of 2.1.[13]

The selectivities of the cations **2** and **11** are low indicating that the cations are unstable. The absolute value of k_{MeOH} is 1.4×10^6 s^{-1} and this allows k_{H_2O} to be calculated for **11** from the ratio of $k_{MeOH} : k_{H_2O}$ and k_{H_2O} was found to be 1.8×10^6 s^{-1}. This value allowed us to calculate the lifetime of cation **11** in water to be 0.55 μs. This oxocyclohexadienylium ion therefore has a similar lifetime to nitrenium ions[14] in water such as 4-ethoxyphenylnitrenium ion which has a lifetime of 0.55 μs.

Reduction of dienones to phenols in propan-2-ol

The solvolysis of **7** in pure methanol gave the corresponding 4-methoxy derivative (**17**) as the sole product after 48 hours (yield by ^1H NMR analysis). The slow solvolysis of **3** and **7** in propan-2-ol did not yield the corresponding 4-isopropoxy trapped product, instead mesitol (**5**) and 2,4,6-tri-*tert*-butylphenol (**6**) were formed respectively. In the case of **7** the yield of phenol was 13% with the remainder being unreacted starting material after 48 hours. The rate of formation of phenol in this solvent was sensitive to solvent polarity. In 50 : 50 acetonitrile–propan-2-ol the yield of the reaction was 26% after 42 hours. In 75 : 25 acetonitrile–propan-2-ol the yield was 49% after 42 hours, reflecting the increased yields as the ionizing power of the medium was increased. The oxocyclohexadienylium ion was not trapped by acetonitrile in a Ritter type reaction.[15] The reduction was suppressed by the addition of competing unhindered nucleophiles such as sodium azide and water, which trapped the cation at the 4-position.

The mechanism of reduction could possibly involve a hydride transfer from the propan-2-ol to the oxocyclohexadienylium ion intermediate forming acetone, followed by aromatisation of the dienone **15** to the phenol **6** (Scheme 5) or by direct hydride transfer to the oxygen. An alternate mechanism involving heterolysis of **3** and **7** to the anion and the bromonium ion is also possible. However, careful ^1H NMR experiments in CD_3CN in a sealed tube with benzene as a marker did not show the presence of any acetone after the reaction had reached completion. There was no formation of bromobenzene or hypobromous products to support the bromonium ion mechanism. In a separate experiment, the bromo compound **7** was also stirred over seven days in 80 : 20 acetonitrile–cyclohexanol. Cyclohexanol was used was used in place of propan-2-ol because its high boiling point (158–162 °C) would prevent the problem of evaporation of the possible ketone product as the experiment proceeded. The reaction was complete with the phenol **6** formed in quantitative yield (by ^1H NMR analysis). 2,4-Dinitrophenylhydrazine was added to trap any cyclo-



Scheme 5

hexanone formed. On work-up, ^{1}H NMR analysis showed that there was no evidence for the formation of the corresponding hydrazone of cyclohexanone. A control reaction of 2,4-dinitrophenylhydrazine with cyclohexanone formed the desired hydrazone as a yellow solid. The demonstration using ^{1}H NMR experiments and the attempted trapping with 2,4-dinitrophenylhydrazine indicate that there was no formation of the corresponding ketones. The reduction of dienone **7** to phenol **6** proceeded in 50 : 50 acetonitrile–*tert*-butyl alcohol in a yield of 20% after 48 hours. The experimental evidence presented here precludes a hydride transfer from the secondary alcohol to the aryloxylium ion as the route to the reduction products, the corresponding phenols.

In summary, the aryloxylium ions **2** and **11** were generated in acetonitrile–water mixtures from precursors **3** and **7**. The aryloxylium ion is an unstable cation with the positive charge effectively located on the *para* position with little delocalisation of charge to other sites as judged by exclusive attack of nucleophiles at the *para* position. This can be attributed to the destabilising effect of the adjacent carbonyl when the positive charge is located on the *ortho* position. The resonance contributor **2c** is therefore more important than either **2b** or **2d**. This is similar to biphenyl-4-ylnitrenium ions where semi-empirical computer models indicate that attack at the *ortho* carbon is thermodynamically favoured but that attack of water shows a kinetic preference for attack at the *para* carbon.[16] The aryloxylium ion may be viewed as a carbonyl-destabilised cation. The instability of the cation is reflected in the low sensitivity to changes in solvent polarity and the small, but significant, common ion rate depression. The $k_{MeOH} : k_{H_2O}$ ratio from competition studies, which was found to be 1.56 and 0.755 for **3** and **7**, is smaller than that observed for other cations[13] and is due to the unstable nature of the cation. The difference in $k_{MeOH} : k_{H_2O}$ between **3** and **7** indicates that trapping by solvent is sensitive to the steric hindrance of the *tert*-butyl group. From the azide trapping experiments $k_{az} : k_{MeOH} = 3610\ M^{-1}$ and $k_{MeOH} : k_{H_2O}$ the lifetime of the cation **11** in water was found to be 0.55 µs. With secondary alcohols, instead of trapping by the alcohol, a slow reduction of **3** and **7** to the phenols **5** and **6** occurs *via* a presumed radical mechanism. Future work will focus on the mechanism of this reduction and on whether aryloxylium ions are trapped by derivatives of guanine as is the case with the arylnitrenium ions.[3]

Experimental

General

Mesitol, 2,4,6-tri-*tert*-butylphenol, potassium bromide and sodium bromide were commercially available and were used without further purification. All solvents were HPLC grade except diethyl ether. Solvents were dried by the standard literature procedures[17] where indicated. The acetonitrile–water mixtures were made from acetonitrile and doubly distilled deionised water. The compositions in the text refer to a ratio of volumes. Stock solutions of **3** and **7** were made up in dry acetonitrile to 0.01 mol dm^{-3}. Kinetics were monitored spectrophotometrically using a Philips PU 8700 spectrophotometer at 251 and 255 nm for compounds **3** and **7** respectively. In all cases the rates were studied under pseudo-first-order conditions by injecting 20 µl of stock solution into 2 cm^3 acetonitrile–water mixtures for a final concentration of *ca.* 10^{-4} mol dm^{-3}. Kinetic experiments were followed for seven half lives and were repeated in triplicate. All rate constants agreed to within ± 5%. In the common ion and azide trap experiments the sodium salt was used in the amounts referred to in the text (Figs. 2 and 3), and constant ionic strength was maintained at 0.10 M and 0.015 M respectively with sodium perchlorate. ^{1}H NMR spectra were recorded at 270 MHz on a JEOL JMN-GX270 FT or a Varian Unity Inova 300 MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane as a reference. Chemical shifts are quoted in ppm and coupling constants in hertz. Infra-red spectra were run on a Galaxy Series FTIR 3000 and the samples were prepared using KBr discs.

4-Bromo-2,4,6-trimethylcyclohexa-2,5-dienone (3)

Mesitol (1.36 g, 0.01 mol) was dissolved in diethyl ether (20 cm^3) and ten drops of pyridine in a 100 cm^3 round-bottom flask. Bromine (0.52 cm^3, 1.2 mol) was dissolved in water (20 cm^3) containing potassium bromide (4.8 g) in a 50 cm^3 flask. The reaction vessel was cooled to −20 °C on an ice–salt–acetone bath. The bromine solution was slowly added to the phenol solution with stirring over five to ten minutes. The reaction mixture initially turned yellow, then orange, as the reaction proceeded. After the addition was complete the reaction mixture was allowed to stir for ten minutes. The reaction was quenched in cold saturated sodium bicarbonate. The organic layer was removed and dried over $MgSO_4$. After filtration the solvent was removed *in vacuo* at 0 °C to give 4-bromo-2,4,6-trimethylcyclohexa-2,5-dienone (**3**) [9] as a yellow solid (1.296 g, 60%); δ_H (270 MHz) 1.91 (3H), 1.94 (6H), 6.87 (2H).

The dienone was made up to 0.01 mol dm^3 in dry acetonitrile and used in experiments within 4 h as it decomposes in solution to 3-bromomesitol, mesitol and 4-bromomethyl-2,6-dimethylphenol.

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (7)

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) was prepared in a similar manner with 2,4,6 tri-*tert*-butylphenol (2.62 g, 0.01 mol) as starting material. After removal of solvent at 0 °C *in vacuo* the solid was recrystallised with petroleum ether (40–60 °C) to give 4-bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) as yellow crystals (1.773 g, 52%); mp 80–81 °C (lit.,[18] 80–81 °C); ν_{max}/cm^{-1} 1659 s (C=O), 1636 s (C=C); δ_H (270 MHz) 1.10 (9H), 1.25 (18H), 6.92 (2H).

4-Hydroxy-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (12)

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) (10.0 g, 0.0293 mol) was dissolved in 60% acetonitrile and 40% water and stirred overnight at 25 °C. The solvent was removed and the white solid was recrystallised in petroleum ether (40–60 °C) to give 4-hydroxy-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**12**) as white needles (7.26 g, 89%); mp 132–134 °C (lit.,[18] 132–134 °C);

ν_{max}/cm^{-1} 3482 s (OH), 1659 s (C=O), 1625 s (C=C); δ_H (270 MHz) 0.98 (9H), 1.24 (18H), 6.59 (2H).

4-Methoxy-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (17)

This compound was prepared by the solvolysis of **7** (5.00 g, 0.0147 mol) in methanol at 25 °C overnight. The solvent was removed to give 4-methoxy-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**13**) as an orange solid. The product was recrystallised in methanol to yield yellow needles (4.13 g, 94%); mp 58–59 °C (lit.,[20] 58–59 °C); ν_{max}/cm^{-1} 2958 s (CH), 1658 s (C=O), 1645 s (C=C); δ_H (270 MHz) 0.95 (9H), 1.20 (18H), 6.54 (2H).

4-Azido-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (16)[21]

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) (1.35 g, 0.0039 mol) was dissolved in dry acetonitrile with excess sodium azide (0.515 g, 0.0079 mol) and stirred overnight (0.843 g, 70%); mp 40–41 °C (lit.,[21] 40–40.5 °C); ν_{max}/cm^{-1} 2096 s (N_3), 1675 s (C=O), 1645 s (C=C); δ_H (300 MHz) 0.90 (9H), 1.26 (18H), 6.59 (2H).

Competition reactions in water–methanol mixtures

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) (0.020 g, 0.0587 mmol) was dissolved in 10 cm^3 80% acetonitrile, 10% water and 10% methanol. The reaction was stirred overnight at 25 °C. The solvent was removed, yielding a solid. A 300 MHz ^{1}H NMR showed the presence of two products, the hydroxy **12** (6.59 ppm) and the methoxy **17** (6.54 ppm); $k_{MeOH} : k_{H_2O}$ was calculated using eqn. (3).

Solvolysis of 7 in propan-2-ol

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) (0.100 g, 0.0587 mmol) was dissolved in 10 cm^3 propan-2-ol. The reaction was stirred for 48 hours at 25 °C. The solvent was removed yielding a solid. A 300 MHz ^{1}H NMR showed the presence of two products, the bromo **7** (6.92 ppm) 87% and the phenol **6** (7.20 ppm) 13%. Yields were calculated by ^{1}H NMR analysis.

Reduction of 7 in acetonitrile–propan-2-ol mixture

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) (0.100 g, 0.029 mmol) was dissolved in 20 cm^3 50 : 50 (and in a separate experiment 75 : 25) acetonitrile–propan-2-ol. The reaction was stirred for 42 hours at 25 °C. The solvent was removed yielding a solid. Both reactions yielded two products, the phenol **6** and starting material **7**. The yield of phenol **6** was 26% in the case of the 50 : 50 mixture and 49% in the case of the 75 : 25 mixture. Yields were determined by ^{1}H NMR analysis of peaks at 7.20 ppm for **6** and 6.92 ppm for **7**.

Reduction of 7 in acetonitrile–*tert*-butyl alcohol mixture

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) (0.100 g, 0.029 mmol) was dissolved in 20 cm^3 50 : 50 acetonitrile *tert*-butyl alcohol. The reaction was stirred for 48 hours at 25 °C. The solvent was removed yielding a solid. The reaction yielded two products, the phenol **6** and starting material **7**. The yield of phenol **6** was 20% with the remainder being unreacted starting material. Yields were determined by ^{1}H NMR analysis of peaks at 7.20 ppm for **6** and 6.92 ppm for **7**.

Competition reactions in water–propan-2-ol mixture

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) (0.075 g, 0.22 mmol) was dissolved in 20 cm^3 of 80 : 20 propan-2-ol–water. The reaction was stirred overnight at 25 °C. The solvent was removed yielding a solid. A 300 MHz ^{1}H NMR showed the presence of three products. The 80 : 20 solvent mixture gave a product ratio of the phenol **6** (5%), starting material **7** (25%) and 4-hydroxydienone **12** (70%). Yields were determined by ^{1}H NMR analysis of peaks at 7.20 ppm for **6**, 6.92 ppm for **7** and 6.59 ppm for **12**.

NMR Studies of propan-2-ol solvolysis

The reaction was followed in a sealed NMR tube. 4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) (0.025 g, 0.0733 mmol) was dissolved in 1 cm^3 d_3-acetonitrile containing propan-2-ol (0.021 cm^3, 0.22 mmol) and benzene (0.013 cm^3, 0.147 mmol). The reaction was followed over 24 hours by analysing the ^{1}H NMR as the reaction proceeded. A 300 MHz ^{1}H NMR showed only one product after 24 hours, the phenol **6** (7.20 ppm). There was no evidence for acetone formation or the products of a bromonium ion.

Reduction of 7 in acetonitrile–cyclohexanol mixtures

4-Bromo-2,4,6-tri-*tert*-butylcyclohexa-2,5-dienone (**7**) (0.129 g, 0.0381 mmol) was dissolved in 20 cm^3 80 : 20 acetonitrile–cyclohexanol. The reaction was stirred over seven days at 25 °C in duplicate. The solvent was removed yielding a solid in the first reaction. A 300 MHz ^{1}H NMR showed the phenol **6** (7.20 ppm) as the sole product. 2,4-Dinitrophenylhydrazine (0.0755 g, 0.0381 mmol) was added to the second reaction mixture and stirred at 25 °C overnight. The solvent was removed yielding a red solid. A 300 MHz ^{1}H NMR did not show any evidence of hydrazone formation. A sample of the hydrazone was prepared (for comparison) as follows. 2,4-Dinitrophenylhydrazine (0.0755 g, 0.0381 mmol) was dissolved in 20 cm^3 80 : 20 acetonitrile–cyclohexanol. Cyclohexanone (0.040 cm^3, 0.0381 mmol) was added to the reaction mixture and the reaction was allowed to stir overnight at 25 °C. The solvent was removed yielding the yellow hydrazone as the sole product. δ_H (300 MHz) 1.80 (6H, m), 2.45 (4H, m), 7.96 (1H, d, $J = 9.37$), 8.28 (1H, dd, $J = 9.665, 2.636$), 9.12 (1H, d, $J = 2.343$).

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