A kinetic EPR study of the dissociation of 1-carbamoyl-1-methylcyclohexa-2,5-dienyl radicals: release of aminoacyl radicals and their cyclisation †

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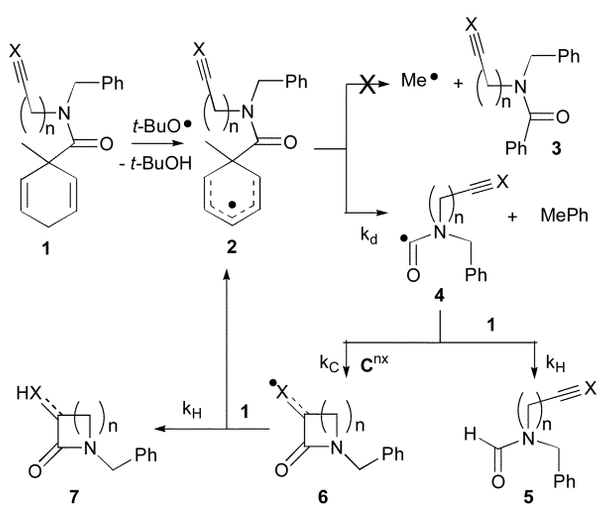
Hydrogen atom abstraction from 1-carbamoyl-1-methylcyclohexa-2,5-dienes generated the corresponding delocalised 1-carbamoyl-1-methylcyclohexa-2,5-dienyl radicals at temperatures below *ca.* 300 K. At higher temperatures suitably substituted examples dissociated to produce toluene and aminoacyl (carbamoyl) radicals. Both types of intermediate were detected and characterised in solution by EPR spectroscopy. From measurements of the concentrations of the initial and released radicals, rate constants and Arrhenius parameters for dissociation of 1-carbamoyl-1-methylcyclohexa-2,5-dienyl radicals were determined. It was found that dissociation to give a secondary aminoacyl radical [$^{\bullet}$C(O)N(R)CH$_2$Ph] took place with a rate constant in the range 50 to 90 s^{-1} at 300 K. The alternative dissociation of the 1-carbamoyl-1-methylcyclohexa-2,5-dienyl radicals to release methyl radicals and an aromatic amide was much slower and did not compete. Analogous dissociations giving primary aminoacyl radicals [$^{\bullet}$C(O)NHR] were significantly slower. Aminoacyl radicals with allyl, butenyl or similar side chains underwent cyclisation and, in the case of the 1,2,2-trimethylbut-3-enyl derivative, cyclisation was faster than dissociation of the parent cyclohexadienyl radical throughout the accessible temperature range. Semi-empirical AM1 and *ab initio* DFT computations indicated the decarbonylations of the aminoacyl radicals did not compete with cyclisations.

Introduction

Several types of functionalised cyclohexadienes have shown promise as new, clean, pro-aromatic reagents for free radical generation. These include esters of 1-methylcyclohexa-2,5-diene-1-carboxylic acid,[1,2] 1-substituted cyclohexa-2,5-diene-1-carboxylic acids,[3,4] silylated cyclohexadienes,[5,6] and 1-carbamoyl-1-methylcyclohexa-2,5-dienes **1**.[7] Hydrogen abstraction takes place selectively from the bisallylic site of **1** to generate a delocalised cyclohexadienyl radical **2** that dissociates by C–C(O) bond scission at moderate temperatures to produce toluene and an aminoacyl (carbamoyl) radical **4**. The released aminoacyl radical may cyclise, if it is suitably unsaturated, and hence be transformed to a new C-centred radical **6** that can abstract hydrogen from more **1**. This constitutes a chain process that has potential for synthetic applications.[8]

The advantages of these cyclohexadienyl amides over organotin reagents, apart from the safety aspect, are that toluene, which can easily be evaporated, is a comparatively benign co-product, and that the H-transfer step is slower. End product analyses showed that competition from an alternative β-scission of radical **2** to afford a methyl radical and an aromatic amide **3**, was insignificant (Scheme 1).

Kinetic information on the chain propagation steps would be very desirable as a tool to facilitate synthetic planning. EPR spectroscopy has proved effective as a method for characterising the intermediates and measuring key rate constants of reactions of cyclohexadienyl derivatives.[9] This paper reports our spectroscopic study of a range of 1-carbamoyl-1-methylcyclohexa-2,5-dienyl radicals, of the characterisation of the released aminoacyl radicals, and of the kinetics of the dissociation steps.



Scheme 1 Formation and reactions of aminoacyl radicals.

Results and discussion

1-Carbamoyl-1-methylcyclohexa-2,5-dienes were prepared from 1-methylcyclohexa-2,5-diene-1-carbonyl chloride and a primary or secondary amine as described previously[7,8] (Scheme 2).

Photolyses of solutions of individual amides **1** and di-*tert*-butyl peroxide (DTBP) in *tert*-butylbenzene solvent, without any additives, gave rise to *tert*-BuOH and toluene together with

† Electronic supplementary information (ESI) available: Selected EPR spectra, measured radical concentrations and the corresponding rate constants at each temperature for each cyclohexadienyl. AM1 computed heats of formation and selected geometric parameters for a series of cyclohexadienyl radicals and dissociation products. UB3LYP computed energies for model aminoacyl radicals. See http://www.rsc.org/suppdata/p2/b2/b206768d/

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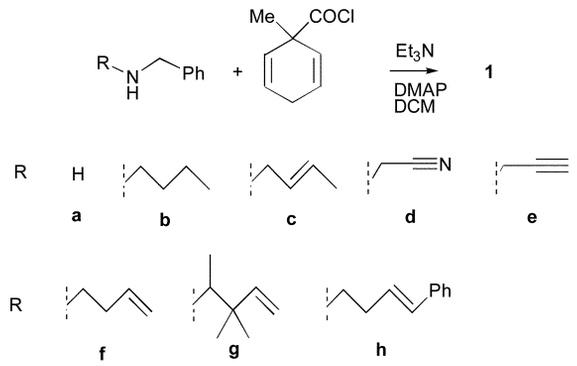

Scheme 2 The series of carbamoylcyclohexadienes studied.

formamides **5**, generally as a mixture of the *cis*- and *trans*-rotational isomers about the C(O)–N amide bond. For the unsaturated amides **1c** and **1e**–**h** the cyclised lactams **7** were also produced. The mechanism and propagation steps under these conditions were as shown in Scheme 1 with chain termination mainly by bimolecular reactions of **2** and **4** ($2k_t$). It has already been shown that the unwanted dissociation of **2** to methyl and aromatic amides **3** is negligible.[7,8] Thus, using the Steady State Approximation, it can easily be shown that eqn. (1) holds assuming, as is usual,[10] that $2k_t$ is essentially the same for all small transient radicals in solution. For low concentrations of amides **1**, or when k_H is small, eqn. (1) simplifies to the more familiar expression (2).[10]

$$k_d/2k_t + k_H/2k_t\{[\mathbf{1}][\mathbf{4}]/[\mathbf{2}]\} = [\mathbf{4}]^2/[\mathbf{2}] + [\mathbf{4}] \quad (1)$$

$$k_d/2k_t = [\mathbf{4}]^2/[\mathbf{2}] + [\mathbf{4}] \quad (2)$$

When solutions of individual amides **1a**–**h** in neat DTBP were photolysed in the resonant cavity of an EPR spectrometer the corresponding cyclohexadienyl radicals **2** were observed over specific temperature ranges. The hyperfine splittings (hfs) and *g*-factors for each radical are recorded in Table 1 and the spectra derived from **1b** are displayed in Fig. 1.

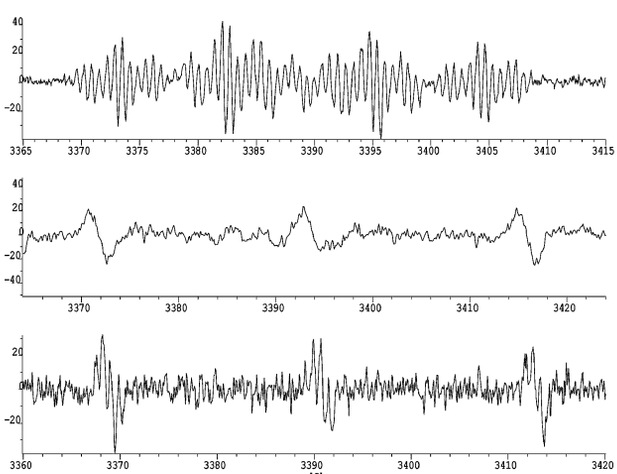

Fig. 1 EPR spectra obtained on photolysis of a solution of **1b** in neat DTBP. Top; cyclohexadienyl radical **2b** at 245 K. Centre; aminoacyl radical **4b** at 345 K. Bottom; radical **4b** under higher resolution at 345 K.

These hyperfine splittings (hfs) were similar to those of other cyclohexadienyl radicals[11] and, as expected, were not very sensitive to the nature of the amide substituent. Small, long-range hfs from the methyl hydrogens and the N-atoms were resolved in most cases. Additional examples of spectra are in the Supplementary Information.† On warming the solutions the spectra of the cyclohexadienyl radicals **2** gradually weakened and were eventually replaced in the case of **2b**,**c** and **f**, usually above *ca.* 310 K, by 3-line spectra having *a*(N) values of 22 ± 1 G (Table 2 and Fig. 1). A few archetype aminoacyl radicals have previously been characterised by EPR spectroscopy,[12–14] and comparison of this literature data with the measured EPR parameters of our higher temperature species (see Table 2) supports our identification of them as aminoacyls **4**. Similarly, DFT computations of the hfs of the $Me_2NC^{\bullet}O$ and *cis*-MeN(H)C$^{\bullet}$O radicals as models (UB3LYP with a 6-31+G(d,p) basis set, Table 2) gave N- and H-atom parameters satisfyingly close to the experimentally measured data for the models and for radicals **4**. These aminoacyl radicals are all capable of existing as *E*- and *Z*-isomers. Separate spectra for the two forms were not, however, observed in any case.

Table 1 EPR parameters for 1-carbamoyl-1-methylcyclohexa-2,5-dienyl radicals **2**[a]

Radical	T/K	H^4	$H^{2,6}$	$H^{3,5}$	Other
2a	260	13.3	9.0	2.6	
2b	245	12.7	9.2	2.6	N 0.66 3H 0.66
2c	250	12.6	9.2	2.7	N 0.62 3H 0.62
2d	250	12.6	9.2	2.9	3H 0.64
2e	250	12.8	9.3	2.6	N 0.64 3H 0.64
2f	250	12.7	9.2	2.7	N 0.65 3H 0.65
2g	250	12.9	9.2	2.8	N 0.71 3H 0.71
2h	245	12.7	9.3	2.7	N 0.64 3H 0.64

[a] Solvent DTBP, all *g*-factors 2.0027 ± 0.0002, hfs in G, 1 mT = 10 G.

Individual components of the aminoacyl N-triplets were rather broad ($\Delta H_{pp} \cong 2.5$ G, see Fig. 1 and Supplementary Information†) and this might be a consequence of overlap of *E*- and *Z*-species with similar *a*(N) values. In one case, aminoacyl **4b** (Fig. 1, bottom) hfs from the four γ-Hs were partly resolved.

Judging by the EPR spectra, **4b**,**c** and **f** are σ-radicals with high barriers to rotation about their N–C(O) amide bonds. Lack of spectral resolution prevented the determination of the *E* : *Z* conformer ratio.

Photolyses of DTBP solutions of **1d** and **1e** gave rise to spectra of **2d** and **2e** at lower temperatures (<300 K). However, the corresponding aminoacyl radicals were not observed at higher temperatures. Instead, spectra having $g = 2.0058$, *a*(N) = 15.2, *a*(4H) = 8.6 G from **1d** and $g = 2.0062$, *a*(N) = 15.5, *a*(2H) = 7.8, *a*(2H) = 9.7 G from **1e** were observed. The EPR parameters indicated that these radicals were nitroxides (aminoxyls, $RCH_2N(O^{\bullet})CH_2Ph$)[14,15] probably derived by oxidation of the corresponding aminyl radicals $RCH_2N^{\bullet}CH_2Ph$ by adventitious traces of oxygen.[16–18] There are several possible ways these aminyl radicals might have been formed. For example, by loss of CO from the aminoacyl radicals **4**. This is unlikely, however, because the phenomenon was only observed with two of the amides and no products derived from the aminyls were detected (see below). Most likely the aminyl radicals were generated by hydrogen abstraction from traces of amines RCH_2NHCH_2Ph remaining from the preparations. The nitroxides have much longer lifetimes than aminoacyls and hence their concentrations build up and dominate EPR spectra. The fact that no products attributable to these species were detected was a good indication that they were formed in only very minor side processes.

In the analogous experiment with the trimethylbut-3-enyl amide **1g** the spectrum of the cyclohexadienyl radical **2g** weakened above 300 K but was replaced by a spectrum consisting of a doublet of triplets [$g = 2.0027$, *a*(2H) = 22.1, *a*(1H) = 29.7 G at

Table 2 EPR parameters for aminoacyl (carbamoyl) radicals[a]

Aminoacyl radical **4**	*T*/K or method	*g*-factor	*a*(N)/G	*a*(Other)/G	Ref.
Me_2NCO	293	2.0019	22.5	6H 0.7	12
Me_2NCO	DFT[b]		23.0	3H −0.5	tw
				3H −0.7	
t-MeHNCO	208	2.0015	21.2	1H 25.1	13
t-MeHNCO	DFT[b]		25.2	1H 23.7	tw
				3H −0.7	
4b	350	2.0019	21.9	4H 0.9	tw
4c	360	2.0019	22.1		tw
4f	330	2.0018	22.1		tw

[a] Solvent for tw = DTBP, tw = this work. [b] Computed by the UB3LYP method with a 6-31+G(d,p) basis set.

340 K; see ESI †]. This spectrum can plausibly be attributed to the *N*-benzyl-4,4,5-trimethyl-2-oxopyrrolidinylmethyl radical **6g**. The *g*-factor and hfs show it to have the structure $^{\bullet}CH_2CHR_2$. Although the observed hfs from the β-H is somewhat greater than that of the cyclopentylmethyl radical [$a(H_\beta)$ = 21.4 G at 300 K][19] the magnitudes of H_β hfs depend critically on the preferred conformation about the C_α–C_β bond and this is strongly influenced by adjacent substituents.[20] The oxo and two close methyl substituents of **6g** will have a major influence on $a(H_\beta)$ so a sizeable difference from cyclopentylmethyl is reasonable. In this case, therefore, the ring closure step was comparatively rapid such that the aminoacyl radical was not detected. Radical **4g** was transformed so quickly to **6g** that the latter was the species detected, *i.e.* cyclisation of **4g** was faster than dissociation of **2g** in the accessible temperature range.

For the *n*-Bu-substituted amide **1b** the concentrations of the cyclohexadienyl radical **2b** and aminoacyl radical **4b** were determined by the EPR method[10] during photolyses of known concentrations of **1b** in DTBP, directly in the EPR resonant cavity. To check for contributions from k_H, samples of **1b** at concentrations of 1.8×10^{-2} and 7.2×10^{-2} mol dm^{-3} were examined in the temperature range 300–340 K. Rate constants k_d were obtained by use of eqn. (2), in conjunction with the well established $2k_t$ value of Schuh and Fischer,[21] corrected for changes in solvent viscosity as described previously.[22] Arrhenius plots of $\log(k_d/s^{-1})$ *vs.* $10^3K/T$ for the two different concentrations were identical to within the experimental error limits (Fig. 2) and therefore H-abstraction from **1** by **4** was negligible

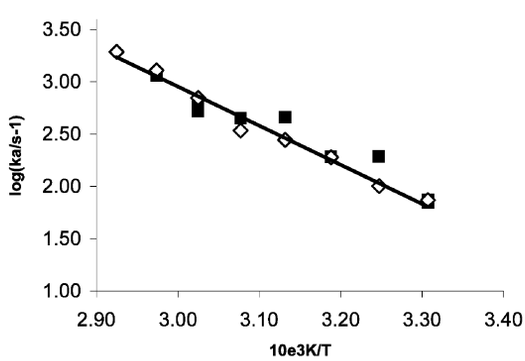

Fig. 2 Arrhenius plots for the dissociation rate constants k_d of radical **2b**. For ◇ [**1b**] = 7.2×10^{-4} and for ■ [**1b**] = 1.8×10^{-4} mol dm^{-3}.

at the amide concentrations employed. Thus, k_H was not experimentally accessible by kinetic EPR.

Similar kinetic EPR experiments were carried out with amides **1c** and **1f**. For **1c** two temperature series using concentrations of 1.8×10^{-2} and 18×10^{-2} mol dm^{-3} were examined and again no contribution from the second term in eqn. (1) was apparent. [Details of the kinetic results are in the ESI †]. The rate constants for aminoacyl extrusion from the but-3-enyl-substituted species **2f** were determined in a similar way. An Arrhenius plot of this data was linear for the lower temperature points but k_d values from runs above *ca.* 340 K were smaller than expected. It is probable that ring closure of radical **4f** became important at these higher temperatures such that the apparent aminoacyl concentrations were lower than the "true" values. Only points in the linear range of the Arrhenius plot for **2f** were used to derive the rate parameters in Table 3.

The only species observed on dissociation of radical **2g** was the cyclised radical **6g**. Rate constants were derived in the same way from measurements of [**2g**] and [**6g**]. Even at the lowest temperature (302 K) cyclisation was fast in comparison with dissociation and therefore the rate constants all relate to dissociation (k_d). However, it follows that $k_C(\mathbf{4g}) \geq k_d \geq 50$ s^{-1} at 300 K and $\geq 2 \times 10^3$ s^{-1} at 350 K. Evidence referred to above indicates that the rate of cyclisation of **4f** was comparable to the rate of dissociation of **2f** at T ≥ 340 K, *i.e.* $k_C(\mathbf{4f}) < 10^3$ at 340 K. The significantly faster cyclisation of **4g** is in accord with expectation, because the bis-methyl substitution of **4g** is expected to increase the cyclisation rate *via* a Thorpe–Ingold type of effect. For comparison, the rate constants for cyclisations of the hex-5-enyl[23] and 2,2-dimethylhex-5-enyl[24] radicals are 2×10^5 and 4×10^6 s^{-1} at 300 K. Rate constants for cyclisations of simple acyl radicals, such as hex-5-enoyl[25] and 2,6-dimethylhex-5-enoyl,[26] are 2.2×10^5 and 1.6×10^5 s^{-1} respectively at 300 K. These are comfortably above the lower limit determined for aminoacyl **4g**. However these rate constants, compared with the observations for **2f** and **2g**, give a hint that aminoacyl cyclisation may be slower than simple acyl cyclisation, possibly because of the thermodynamic stability of the amide bonds in the former.

Radical **2h** gave a well-resolved spectrum (Table 1) and on increasing the temperature this spectrum weakened, eventually beyond detection at *ca.* 350 K. However, neither the aminoacyl radical **4h** nor the cyclised radical **6h**, were detected. This is probably because the cyclised radical **6h** is a delocalised benzyl type with an EPR spectrum consisting of so many narrow lines (72) that individual components were below the threshold of detection.

Table 3 shows that the measured rate constants for dissociation of **2b**,**c**,**f**,**g** were all rather similar. Within the narrow substituent range studied, the rate of extrusion of $^{\bullet}CON(Bn)R$ from **2** was almost independent of R. However, extrusion of primary aminoacyl radicals $^{\bullet}CONHR$ was significantly slower. Data for extrusion of *n*-Pr$^{\bullet}$ from the 1-*n*-propylcyclohexa-2,5-dienyl-1-carboxylic acid radical (**8**)[7] are included for comparison purposes. This indicated that extrusion of an aminoacyl radical was 3 to 4 times faster than extrusion of *n*-Pr$^{\bullet}$ at 300 K. The temperature ranges of individual experiments were quite short (40 ± 10 K) and hence accurate *A*-factors could not be obtained with this technique because of the long extrapolations involved. Deviations from the 'normal' value for unimolecular processes [$\log(A/s^{-1})$ = 13] were not gross, hence it is probable that the true *A*-factors are all close to this. The final column of Table 3 shows activation energies standardised to assumed $\log(A_d/s^{-1})$ factors of 13.

The structures and energies of two representative amidocyclohexadienyl radicals, some related species, and their dissociation products, were computed using the AM1 semi-empirical

Table 3 Kinetic data for dissociation of amidocyclohexadienyl radicals **2** and related radicals[a]

Process	T range/K	k_d/s^{-1} (300 K)	log(A_d)/s^{-1}	E_d	E_d[13][b]
2a ⟶ **4a**	>350	<8	[13][c]		>72
2b ⟶ **4b**	302–342	60	13.3	66.2	64.2
2c ⟶ **4c**	310–370	90	11.8	56.1	63.8
2f ⟶ **4f**	308–348	80	10.1	47.0	65.0
2g ⟶ **6g**	302–336	49	12.4	61.4	65.1
8 ⟶ *n*-Pr[d]		22	13.0	66.9	66.9
8 ⟶ CO_2H[d]		1.7	[13][c]		73.2

[a] Activation energies in kJ mol^{-1}. [b] Standardised activation energies assuming log[A_d/s^{-1}] = 13. [c] Assumed value. [d] Data from ref. 7; **8** is the 1-*n*-propylcyclohexa-2,5-dienyl-1-carboxylic acid radical.

Table 4 AM1 computed reaction enthalpies and activation energies for cyclohexadienyl radicals[a]

CHD radical[b] 1-substituents	Products	ΔH_o(-COX)	$E^{\ddagger}$(-COX)
(Me)CONMe$_2$	PhMe + CONMe$_2$	0.8	79.0
(Me)CONHMe	PhMe + CONHMe	21.7	74.4
(Me)COOMe	PhMe + COOMe	64.8	105.3
(Me)COOH	PhMe + COOH	66.5	109.9
(Pr-*n*)COOH	PhPr-*n* + COOH	66.0	90.3

[a] Enthalpies and energies in kJ mol^{-1}. [b] CHD = cyclohexa-2,5-dienyl, R = Me or *n*-Pr.

		ΔH_o(-R)[b]	$E^{\ddagger}$(-R)[b]
Me(CONMe$_2$)	PhCONMe$_2$ + Me	93.6	117.9
Me(CONHMe)	PhCONHMe + Me	103.7	116.2
Me(COOMe)	PhCOOMe + Me	130.0	116.4
Me(COOH)	PhCOOH + Me	85.3	114.5
Pr-*n*(COOH)	PhCOOH + *n*-Pr	50.2	84.0

SCF MO method.[27] All structures were fully optimised with respect to all geometric variables. The rings of radicals **2** were computed to be planar with C(1)–C(O)NR$_2$ bond lengths of *ca.* 1.55 Å, *i.e.* as long as the longest computed for C(1)–alkyl in the analogous 1-alkylcyclohexa-2,5-dienyl-1-carboxylic acid radicals.[9] The computed enthalpies of reaction (ΔH_o) for both modes of dissociation are listed in Table 4.

The transition states (TS) for dissociation were also examined using the AM1 method. For loss of C(O)X radicals (X = NR$_2$, OR, or OH) the rest of the TS structures (*i.e.* the rings and other substituents) were only 10 to 15° from planar and the leaving radical subtended an angle close to 90° with the "plane" of the rest of the structure. The ring C(1)···C(O)X bond lengths were 2.00 ± 0.03 Å in the TS of the dissociations of the carbamoyl-substituted radicals. Similar structures were computed for loss of the methyl radical, the ring C(1)···Me distances being slightly longer at 2.11 and 2.14 Å. The computed activation energies for release of the aminoacyl radicals were in quite good agreement with experiment (compare Table 4 and Table 3 last column). The computed ΔH_o values indicate $^{\bullet}$C(O)NMe$_2$ loss is almost thermoneutral but $^{\bullet}$C(O)NHMe loss is more endothermic, in agreement with the experiment. The corresponding computed activation energies for these two processes were, however, very similar. Experimental rate data is not available for release of $^{\bullet}$COOMe, but previous EPR experiments[2,7] showed the activation energies must be higher than for aminoacyl release, also in agreement with the computations. Similarly, Table 4 shows that the computed ΔH_o and $E^{\ddagger}$ values for release of Me$^{\bullet}$ both indicate this dissociation to be much less favourable than aminoacyl loss; in good agreement with experiment.

Enthalpies [ΔH_o] for the decarbonylation reactions of model aminoacyl radicals viz:

$$^{\bullet}C(O)NRMe \longrightarrow CO + {}^{\bullet}NRMe \qquad (3)$$

were computed by semi-empirical AM1 and *ab initio* DFT methods (Table 5). Agreement between the two methods was poor but, as judged by the far more reliable DFT results, CO loss should be much more endothermic than dissociation of the parent carbamoylcyclohexadienyl radicals (compare Table 4, top 2 rows). Thus, decarbonylations of radicals **4** are unlikely to be significant in the temperature range studied. The comparatively moderate endothermicities, computed by the DFT method, do however suggest, that decarbonylation could become important at higher temperatures. Our conclusion (see above), that the nitroxide radicals detected from reactions of **1d**,**e** did not owe their formation to decarbonylations of aminoacyl radicals **4d**,**e**, appears to be sound.

Conclusions

1-Carbamoyl-1-methylcyclohexa-2,5-dienyl radicals dissociate cleanly at temperatures above *ca.* 340 K to generate aminoacyl radicals together with toluene. The alternative dissociation to release a methyl radical and an aromatic amide does not occur. It was found that dissociation to give a secondary aminoacyl radical ($^{\bullet}$C(O)N(R)CH$_2$Ph) took place more efficiently than analogous dissociation to give a primary aminoacyl radical ($^{\bullet}$C(O)NHR). Aminoacyl radicals with allyl, butenyl or similar side chains underwent 4-*exo*- or 5-*exo*-cyclisations and, in the case of the 1,2,2-trimethylbut-3-enyl derivative, 5-*exo*-cyclisation was faster than dissociation of the initial delocalised cyclohexadienyl radical throughout the accessible temperature range. Decarbonylations of the aminoacyl radicals did not compete with cyclisations. Semi-empirical AM1 and *ab initio* UB3LYP computations indicated the decarbonylation to be endothermic. Thus 1-carbamoyl-1-methylcyclohexa-2,5-dienes containing secondary amide groups are good aminoacyl precursors and can potentially function in radical chain mediated preparations of β- and γ-lactams.

Experimental

Amides **1a**–**h** were prepared as described previously.[7,8] Commercial DTBP was passed down a column of dry neutral

Table 5 Computed enthalpies for decarbonylations of aminoacyl radicals

Decarbonylation reaction	ΔH_o/kJ mol^{-1} AM1	ΔH_o/kJ mol^{-1} UB3LYP[a]
(3) R = H	154.2	69.5
(3) R = Me	115.8	50.2

[a] 6-31+G(d,p) basis set: values include ZPVE and thermal energy correction to 298 K.

alumina and then distilled under reduced pressure. EPR spectra were obtained with a Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation. Samples of the substrate (0.3 to 40 mg) and DTBP (0.01 to 0.5 cm^3), or *tert*-butylbenzene (up to 0.5 cm^3), in 4 mm od quartz tubes, were de-aerated by bubbling nitrogen for 20 min, and photolysed in the resonant cavity by unfiltered light from a 500 W super pressure mercury arc lamp. For reactions performed in cyclopropane, the solution was degassed on a vacuum line using the freeze–pump–thaw technique, and the tube was flame sealed. In all cases where spectra were obtained, hfs were assigned with the aid of computer simulations using the Bruker Simfonia software package. For kinetic measurements, amide samples were used in 'single shot' experiments, *i.e.* new samples were prepared for each temperature and each acid concentration, to minimise sample depletion effects. EPR signals were double integrated using the Bruker WinEPR software and radical concentrations were calculated by reference to a known concentration of DPPH, as described previously.[22]

Quantum chemical calculations

For the aminoacyl radicals $^{\bullet}CONR_2$ quantum chemical calculations were carried out with the Gaussian 98W package.[28] Density functional theory, UB3LYP variant, was employed. The equilibrium geometries were fully optimised with respect to all geometric variables, no symmetry being assumed, with the 6-31+G(d,p) basis set. Isotropic hfs were obtained from Fermi contact integrals as listed in the Gaussian 98 output. For the calculation of thermodynamic properties the computed vibrational frequencies were scaled by the recommended[29] factor of 0.9614. Total energies were adjusted for zero point vibrational energies and for thermal corrections to 298 K. The structures and energies of the cyclohexadienyl radicals, and their dissociation products, were also computed using the AM1 semi-empirical SCF MO method,[27] implemented with the HyperChem software package (version 5.1).[30] All structures were fully optimised with respect to all geometric variables. The RHF and UHF options were used for closed shell molecules and open shell radicals respectively. (Heats of formation of individual species, together with limited structural data, are given in the ESI †).

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