Conformational Analysis of Imidoyl Radicals by Electron Spin Resonance Spectroscopy

Alwyn G. Davies,* Jean-Yves Nedelec, and Roger Sutcliffe
Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ

A series of *N*-t-butylimidoyl radicals, $R\dot{C}{=}NBu^t$, have been prepared by the reaction of t-butoxyl radicals with the parent imines, $RCH{=}NBu^t$, and their e.s.r. spectra have been recorded. The n.m.r. coupling constants, $^3J(CH{-}CH{=}NBu^t)$, in the imines are related to the e.s.r. hyperfine coupling constants, $a(H_\beta)$, in the imidoyl radicals by the expression $a(H_\beta)/G = 3.53\ ^3J(CHCHNBu^t)/Hz - 8.48$. A similar relationship has been identified previously between the aldehydes and the acyl radicals.

These results are rationalised on the assumption that the radicals have a σ-electronic configuration, and that similar intramolecular interactions in the imines and imidoyl radicals impose on them similar conformations.

We have shown previously that a linear relationship [equation (i)] exists between the n.m.r. coupling constants, $^3J(HC{-}CHO)$, of aldehydes (1) and the e.s.r. coupling constants, $a(H_\beta)$ in the corresponding σ acyl radicals (2).[1]

$$a(H_\beta)/G = 2.20\ ^3J(HC{-}CHO)/\mathrm{Hz} - 1.98 \qquad \text{(i)}$$

Theoretical calculations show that $a(H_\beta)$ and $^3J(HC{-}CHO)$ should show a similar type of angular dependence on the conformation about the C(α)–C(β) bond, being maximum when the dihedral angle, θ, is 180° and minimum when θ = 90°, rising slightly when θ is between 90° and 270° (Scheme 1).

Equation (i) was therefore interpreted to imply that intramolecular interactions in the parent aldehyde (1) and the product acyl radical (2) were similar, so that the aldehyde and acyl radical have similar structures, and, in particular, similar conformations about the C(α)–C(β) bond.[1] No relationship of this type exists with the alkyl radicals, because they usually have π configurations, and their formation from their precursors is accompanied by $sp^3 \longrightarrow sp^2$ rehybridisation.

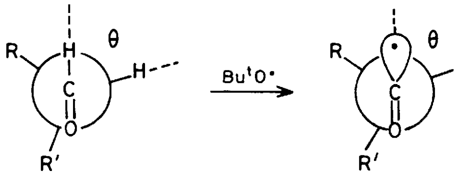
Particular classes of acyl radicals which support this analysis are the propenoyl radicals, which like the corresponding aldehydes, are most stable in the *s-trans*-conformation,[1] and the cyclopropylacyl, oxiranylacyl, and aziridin-2-ylacyl radicals which, like the corresponding aldehydes, are most stable when the plane containing the acyl moiety bisects the three-membered ring.[2]

We report here a study of the e.s.r. spectra of the imidoyl radicals (4) in an attempt to identify a correlation similar to that of equation (i) between the value of $a(H_\beta)$ in the radicals and $^3J(CHCH{=}NR'')$ in the parent imines (3) (Scheme 2).

The e.s.r. spectra of a few imidoyl radicals prepared as in Scheme 2 have been reported ($R'' = Bu^t$, R = H, R′ = Me, Et, Bu,[3] or H[4]); the low *g* factors (*ca.* 2.0016) and low values of $a(H_\beta)$ were interpreted to imply a σ-electronic configuration.[3] Further examples have been prepared by the addition of the radicals $R''^{\bullet}$ (*e.g.* $Me_3SiO^\bullet$, $Me_3CO^\bullet$, $MeS^\bullet$, $Et_3Si^\bullet$, and $Ph^\bullet$, but not alkyl) to isonitriles, particularly $Bu^tN{=}C\colon$.[4] When $R'' = Me_3SiO$ or Me_3CO, the high value of $a(^{13}C_\alpha)$ (*ca.* 100 G) in the imidoyl radicals confirmed their σ-configuration, but when R″ was less electronegative (*e.g.* Et_3Si), $a(^{13}C_\alpha)$ was much smaller, implying that the unpaired electron resides in an orbital of mainly π-character.[4]

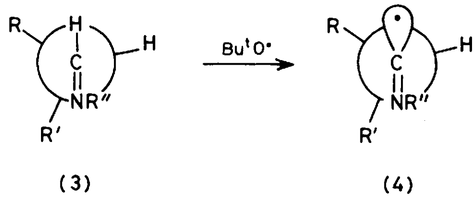
Results and Discussion

Attention was concentrated on the *N*-t-butylimines (3; $R'' = Bu^t$), because the t-butyl group has a low reactivity towards t-butoxyl radicals, and, because of its bulk, it should impose a *trans*-configuration about the C=N bond in the imines (3) and the imidoyl radicals (4). However, a few experiments with *N*-propylimines gave concordant results.



(1) (2)

Scheme 1.



(3) (4)

Scheme 2.

Mixtures of the imines and di-t-butyl peroxide in cyclopropane as solvent were irradiated in the cavity of an e.s.r. spectrometer. Frequently the samples, before photolysis, showed the spectrum of the di-t-butylnitroxyl radical [a(N) *ca.* 15.2 G], but when the sample was irradiated, this spectrum rapidly disappeared and was replaced by the spectrum of the appropriate imidoyl radical. The lines were always broad (0.8—1.5 G), though no broader than those of the corresponding acyl radicals; a typical spectrum is shown in Figure 1.

The results are presented in the Table. The values of $^3J(HC{-}CH{=}NBu^t)$ is given for the parent imine in carbon tetrachloride at 37 °C. The hyperfine coupling to nitrogen in the radicals was low (1.75—2.4 G) and independent of temperature, but the proton hyperfine coupling constant, $a(H_\beta)$, was always temperature dependent, and values are given for the extremes of the temperature range over which measurements could be made, and for one intermediate temperature.† In Figure 2,

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† For the acyclic acyl radicals (2), well resolved spectra could usually not be obtained over a sufficient range of temperature for $da(H_\beta)/dT$ to be determined, but if, as we believe, the value of $a(H_\beta)$ is dominated by the time-averaged value of the dihedral angle θ, $a(H_\beta)$ should approach the value for the acetyl radical (4.0 G) at high temperatures.

Table. N.m.r. coupling constants of imines,[a] and e.s.r. spectra of the corresponding imidoyl radicals[b]

No.	$^3J(CH\text{-}CH{=}N)$/Hz	$a(H_\beta)$/G	a(N)/G	ΔH_{pp}/G	T/K	g
	$RCH{=}NBu^t$ and $R\dot{C}{=}NBu^t$					
1 CH_3	4.67	8.55	1.75		173	2.0016[c]
2 CH_3CH_2	4.11	5.1	1.85	1.0	154	2.0015
		5.6	1.85		190	
		5.9	1.85		227	
3 $CH_3[CH_2]_2$	4.33	6.5	1.8	1.0	163	2.0014
		6.7	1.8		179	
		7.0	1.8		222	
4 $CH_3[CH_2]_3$	4.33	6.2	1.9	1.0	157	2.0014
		6.5	1.9		177	
		7.0	1.9		218	
5 $CH_3[CH_2]_4$	4.44	6.4	1.9	1.5	152	2.0015
		6.7	1.9		190	
		6.9	1.9		224	
6 $CH_3[CH_2]_6$	4.44	6.5	1.9	1.0	157	2.0015
		6.7	1.9		201	
		7.1	1.9		237	
7 Me_2CHCH_2	4.67	7.3	2.0	1.0	160	2.0015
		7.6	2.0		201	
		7.9	2.0		242	
8 Me_3CCH_2	5.11	9.7	2.0	1.0	171	2.0015
		9.5	2.0		213	
		9.2	2.0		238	
9 Me_2CH	4.40	6.8	1.8	0.8	144	2.0016
		7.0	1.8		163	
		7.1	1.8		182	
10 $\overline{CH_2CH_2CH}$	6.3[d]	16.0	2.4	1.0	163	2.0015
		14.3	2.4		200	
		12.8	2.4		273	
11 Me_3C			1.8	1.0	173	2.0015
12 Ph[e]					210	2.0015
13 $PhCH_2$	4.2	*f*				
14 PhCH=CH	4.9	*f*				
	$RCH{=}NPr$ and $R\dot{C}{=}NPr$					
15 $CH_3[CH_2]_3$	4.45	6.6	1.4		172	2.0014
		6.7	1.4		183	
16 $CH_3[CH_2]_8$	4.2	6.4	1.4		152	2.0014
		6.7	1.4		190	
		7.0	1.4		224	

[a] In CCl_4 at 310 K; solubilities were too low to permit the temperature dependence to be determined. [b] In cyclopropane. [c] Ref. 3. [d] Temperature dependence (T/K, J/Hz): 243, 7.5; 273, 7.0; 308, 6.3; 343, 6.2. [e] Above 220 K, the spectrum of the t-butyl radical was also observed. [f] No interpretable spectra were obtained.

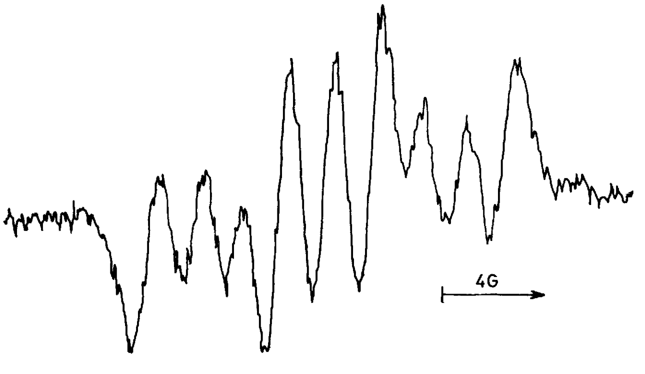


Figure 1. E.s.r. spectrum of the radical $Et\dot{C}{=}NBu^t$ obtained from the photolysis of a solution of di-t-butyl peroxide and *N*-t-butylpropylideneamine in cyclopropane at −102 °C

values of $^3J(HC\text{-}CH{=}NBu^t)$ for the imines at 37 °C are plotted against values of $a(H_\beta)$ for the corresponding imidoyl radicals at −50 °C, giving a regression line described by equation (ii).

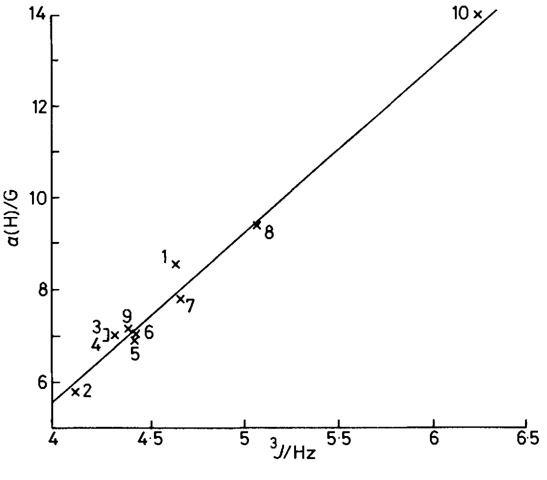


Figure 2. Plot of $^3J(CHCHNBu^t)$ in imines, $RCH{=}NBu^t$, against $a(H_\beta)$ in the corresponding imidoyl radicals, $R\dot{C}{=}NBu^t$; points are numbered to correspond with the serial numbers of the compounds in the Table

These temperatures were dictated by the conditions under which good quality n.m.r. and e.s.r. spectra could be obtained. We attempted to record n.m.r. spectra at the same low temperatures as the e.s.r. spectra, but the imines were not sufficiently soluble in carbon tetrachloride. The intercept which the plot makes with the axis may derive in part from the fact that the parameters Q and J relate to different temperatures, but this is unlikely to be able to account for the whole of the effect.

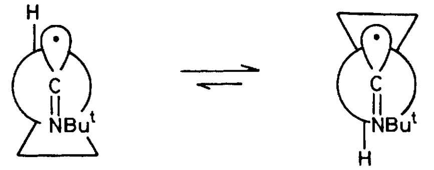
$$a(\mathrm{H}_\beta)/\mathrm{G} = 3.53 \times {}^3J(HC\text{–}CH\text{=}\mathrm{NBu^t})/\mathrm{Hz} - 8.48 \quad \text{(ii)}$$

These results can be rationalised if it is accepted that the *N*-alkylimidoyl radicals have a σ-electronic configuration; the direct evidence for this, *i.e.* the value of $a(^{13}\mathrm{C}_\alpha)$, is as yet lacking because the e.s.r. spectra are too weak for this parameter to be determined without isotopic enrichment, but it is in accord with indirect evidence.[3,4] The relation [equation (ii)] between $^3J(CH\text{–}CH\text{=}\mathrm{NBu^t})$ in the imines and $a(\mathrm{H}_\beta)$ in the imidoyl radicals, and their parallel dependence on temperature, is then interpreted in the same way as the relation [equation (i)] between the corresponding parameters in the aldehydes and the acyl radicals: [1] the imines (3) and the imidoyl radicals (4) have similar conformations about the C(α)–C(β) bond, and the n.m.r. and e.s.r. coupling constants obey a similar type of dihedral angular dependence.

The conformational implications of these e.s.r. hyperfine coupling constants in the imidoyl radicals are rather unclear because less work has been carried out on the n.m.r. spectra and conformations of imines than has been done on the corresponding aldehydes.[5] Karabatsos and Hsi [6] showed that, in the *O*-methyl oximes (3; R″ = OMe), $^3J(CH\text{–}CH\text{=}\mathrm{NOMe})$ is normally greater in the higher oximes than in acetaldehyde oxime, and shows a negative temperature coefficient, and they concluded that the most stable conformation was that in which a β-C–H bond eclipsed the C=N bond. In our imines, however, (3; R″ = Bu^t), $^3J(CH\text{–}CH\text{=}\mathrm{NBu^t})$ is usually *less* for the higher derivatives than the $\mathrm{CH_3CH{=}NH}$, and would presumably show a positive temperature dependence as rotation becomes more free at higher temperatures. The relative magnitudes, and their presumed temperature dependence, of ^3J in the *N*-t-butylimines, are closer to those in the aldehydes than in the *O*-methyl oximes, and the values of $a(\mathrm{H}_\beta)$ in the imidoyl radicals correlate reasonably well with those in the corresponding acyl radicals.

Two of the imines, $\mathrm{Me_3CCH_2CH{=}NBu^t}$ and $\overline{\mathrm{CH_2CH_2C}}\mathrm{H\text{-}CH{=}NBu^t}$, were exceptional in that they and their derived radicals showed coupling constants larger than those of *N*-t-butylethylideneamine and its radical. In the former compound, the bulky $\mathrm{Me_3C}$ group is presumably sterically repelled by the $\mathrm{NBu^t}$ group so that the $\mathrm{CH_2}$ hydrogen atoms spend a larger proportion of the time near to the position *trans* to the CH bond in the imine, or the singly occupied σ-orbital in the radical, where coupling is most effective.

The cyclopropylmethyleneamine and imidoyl radical may differ from the other derivatives discussed here in that, like the corresponding aldehyde and acyl radical,[2] they have a two-fold rather than three-fold barrier to rotation about the C(α)–C(β) bond. The magnitude and the temperature dependence of ^3J in the imine and of $a(\mathrm{H}_\beta)$ in the radical would then be consistent with the most stable conformation being that in which the β-C–H bond eclipses the $\mathrm{C{=}NBu^t}$ group; this is illustrated for the radical in Scheme 3.



Scheme 3.

If this is correct, the barrier to the rotation must be substantially less than the 17.5 kJ mol^{-1} which is observed in the cyclopropylacyl radical, as there was no detectable effect on the linewidth, nor any observation of the two individual rotamers down to 163 K; with the cyclopropylacyl radicals, the individual spectra can be detected up to 186 K.

Experimental

The preparations of the aldehydes have already been described.[1,2] The following example illustrates the method by which the aldehydes were converted into the t-butylimines; it is important that the aldehyde should be added very slowly to the amine, rather than *vice versa* at 0 °C, to avoid polymerisation.

N-*t-Butylpentylideneamine*.—Pentanal (2.6 g) was added, with stirring, during 45 min, to t-butylamine (2.19 g) at 0 °C, and the mixture was then stirred for a further 20 min. Potassium hydroxide pellets were added to separate the organic and aqueous layers, and the organic layer was then dried overnight over more KOH in the refrigerator. Next day, the organic layer was distilled, giving the imine, b.p. 52 °C at 18 mmHg; it polymerised during 4 days at room temperatures, but was stable at −20 °C.

All the imines showed satisfactory i.r. and n.m.r. spectra. Values for $^3J(CHCH\mathrm{NR})$ are given in the Table.

E.s.r. Spectroscopy.—Solutions of the imines and di-t-butyl peroxide in cyclopropane as solvent were sealed under vacuum in Suprasil silica tubes, and irradiated in the cavity of a Varian E4 spectrometer, with light from a high-pressure mercury arc, as described previously.[1]

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