The Electron Spin Resonance Spectra of Cyclopropylacyl Radicals: Spectroscopically Distinguishable σ-Radicals Related by Rotation about a Single Bond

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Summary Below -90 °C, cyclopropylacyl radicals show two e.s.r. spectra which are associated with the two conformers, of approximately equal stability, in which the plane containing the acyl group bisects the cyclopropyl ring, with a two-fold rotational barrier of about 17·5 kJ mol^{-1}.

THE relationship between conformation, stability, and e.s.r. hyperfine coupling has been thoroughly investigated for carbon-centred π-radicals,[1] but not for σ-radicals. We report here a study of this relationship for the cyclopropylacyl radical, which provides the first example of isomeric σ-radicals related by rotation about a formal single bond.

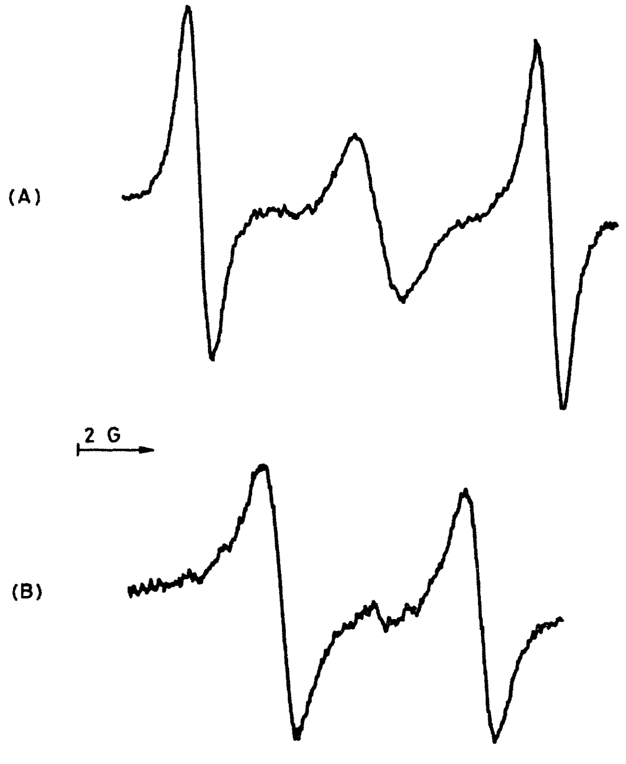
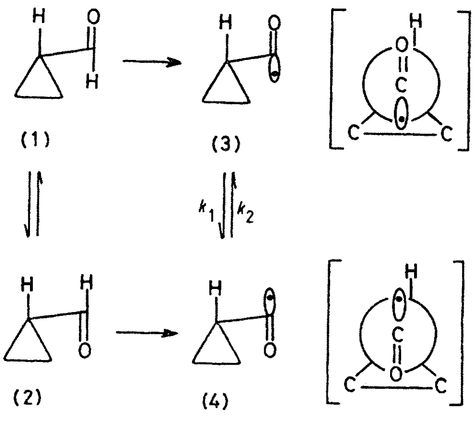


FIGURE. The e.s.r. spectra of the cyclopropylacyl radical. (A) At -101 °C. (B) At -38 °C; the distortion in the centre of this spectrum is due to a cavity signal.

The radicals were generated in the e.s.r. cavity, in cyclopropane solution, by the photolysis of di-t-butyl peroxide in the presence of cyclopropanecarbaldehyde, or of hexabutylditin in the presence of cyclopropylcarbonyl bromide,† or, in dichlorodifluoromethane solution, by the photolysis of cyclopropyl t-butyl ketone.‡

Below -90 °C, the spectra of two radicals were observed, one consisting of a widely spaced doublet, and the other of a broad singlet, each with further hyperfine splitting, as shown in the Figure (A). Within an experimental error of about ±5%, the relative concentrations of the two radicals at -101 °C from each of the three sources was 60:40. As the temperature is raised through -90 °C, the lines broaden then resolve into the doublet shown in the Figure (B).

The g-factors and the ^{13}C hyperfine coupling constants unambiguously identify both radicals as σ-acyl radicals. Electron diffraction,[2] microwave,[3] and proton n.m.r. spectra[4] establish that cyclopropylcarbonyl compounds are most stable in the conformations (**1**) and (**2**) in which the plane containing the carbonyl group bisects the cyclopropyl ring, and we identify the two radicals with the corresponding conformers (**3**) and (**4**). This assignment is supported by INDO calculations of the hyperfine coupling constants. Details of the observed and calculated spectra are given in the Table.



Above *ca.* -90 °C, rotation about the C_α–C_β bond is rapid on the e.s.r. time scale, and a time-averaged spectrum is observed. Computer simulation of the spectra in the region of intermediate rates of exchange gives the approxi-

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† This method for the observation of the e.s.r. spectra of acyl radicals has not been reported previously.

‡ Photolysis of the ketone showed also the spectrum of the t-butyl radical.

TABLE. Observed and calculated e.s.r. spectra of cyclopropylacyl radicals (**3**) and (**4**).

Radical		Hyperfine coupling constants/G				g	T/°C
		$a(H_\beta)$	$a(^{13}C_\alpha)$	$a(2H_\gamma)$	$a(2H_\gamma')$		
(**3**)	Obs.	18·2	120·5	0·2	—	2·0009	−101
	Calc.[a]	25·2	125·0	0·25	0·02		
(**4**)	Obs.	0·5 [b]	123·6	0·95 [b]	0·6 [b]	2·0008	−101
	Calc.[a]	−0·2	124·5	2·5	0·8		

[a] Assuming ∠C–C=O = 122°, and a normal geometry for the rest of the molecule. [b] Tentative analysis based on computer simulation.

mate values at −87 °C of k_1 1·8 × 10^7 s^{-1}; k_2 2·6 × 10^7 s^{-1}, E_a 17·5 kJ mol^{-1}, A 3·2 × 10^{12} s^{-1}; and ΔG_2 500 J mol^{-1}.

These values are to be compared with those which have been obtained for the parent aldehyde of E_a ($\mathbf{1}\rightleftharpoons\mathbf{2}$) $\nless$ 10·5 kJ mol^{-1} (from electron diffraction)[2] or 18·4 ± 1·7 kJ mol^{-1} (from microwave spectroscopy),[3] and ΔH^0 ($\mathbf{1}\rightarrow\mathbf{2}$) 6·3 kJ mol^{-1} (from proton n.m.r. spectroscopy).[4]

The origin of the two-fold barrier to rotation in both the radical and its aldehyde precursor is probably best understood in terms of the interaction between the carbonyl π-orbital and a Walsh π-orbital of the cyclopropyl ring.[2,3]

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