The Electron Spin Resonance Spectra of Saturated and Unsaturated Acyl Radicals

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Summary Saturated and unsaturated aldehydes react with t-butoxyl radicals in fluid solution to show strong well resolved e.s.r. spectra of the corresponding σ-acyl radicals with the same conformations as the parent aldehydes.

The e.s.r. spectra of only a few acyl radicals have been observed in fluid solution:[1] the lines are usually reported to be broad, and hyperfine couplings to the β-protons are small or unresolved,† and this has perhaps discouraged further studies. We report here that this reputation is misleading: many (and perhaps most) acyl radicals show sharp, well resolved spectra, and, in particular, the 2,3-unsaturated acyl radicals, which have not previously been reported, show substantial hyperfine couplings.

The acyl radicals were generated by photolysis of di-t-butyl peroxide in the presence of the appropriate aldehyde in cyclopropane solution. Details of the experimental

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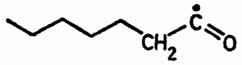
† The spectra of the radicals Me$\dot{C}$O, Et$\dot{C}$O, Pr$^i\dot{C}$O, and Bu$^t\dot{C}$O (derived from photolysis of isopropyl or t-butyl ketones) are reproduced in H. Paul and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1575. The peak-to-peak line widths (ΔH_{pp}) of the first-derivative spectra are *ca.* 5 G, and hyperfine coupling is apparent only for the Me$\dot{C}$O radical, where $a(3H_\beta) = 4{\cdot}0$ G.

spectra are given in Table 1, and of INDO calculations on relevant structures in Table 2. The spectra of the radicals (**1**—**3**) are typical of those which we have obtained for larger acyl radicals which are not conjugatively unsaturated.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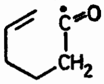
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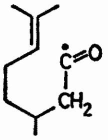
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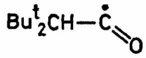
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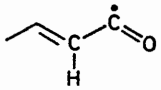
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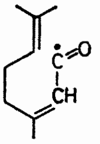
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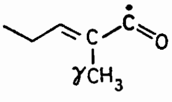
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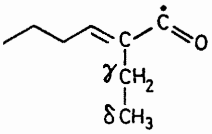
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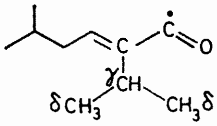
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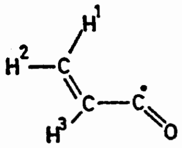
TABLE 1. E.s.r. spectra of acyl radicals

	$a(H_\beta)$/G	$a(H\gamma)$/G	g	ΔH_{pp}/G	T/°C
(**1**)	2·18 (2H)	—	2·0005	0·7	−52
(**2**)[a]	—	—	2·0006	2·05	−89
(**3**)[a]	3·06 (1H)	—	2·0004	1·4	−126
	2·40 (2H)	—	,,	1·1	−60
(**4**)[b,c]	11·2 (1H)	—	2·0005	1·0	−116
(**5**)[d,e]	19·5 (1H)	—	2·0005	0·9	−119
(**6**)[a]	19·8 (1H)	—	2·0005	1·2	−126
(**7**)	—	1·10 (3Hγ)	2·0005	0·4	−119
(**8**)	—	2·22 (2Hγ)	2·0003	0·9	−122
		2·1 (2Hγ) 0·5 (3Hδ)	,,	0·3	−68
(**9**)	—	7·7 (1Hγ)	2·0005	1·35	−117
		7·4 (1Hγ) 0·4 (6Hδ)	,,	0·2	−81

[a] No ring-closure of the radicals was apparent. Z. Čekovic (*Tetrahedron Letters*, 1972, 749) reports products arising from ring closure of the radicals (**2**) and (**3**). [b] $a(^{13}C)$ 114·6 G. [c] The same radical has been observed from the photolysis of HI in the presence of di-t-butylketen; $a(H_\beta)$ 10·7 G at −70 °C: V. Malatesta, D. Forrest, and K. U. Ingold, *J. Phys. Chem.*, 1978, **82**, 2370. [d] Acrolein and methacrolein showed only the spectrum of radicals resulting from the addition of the t-butoxyl radical to the C=C bond. [e] Ceric photosensitization of crotonaldehyde in the solid state at 77 K is reported to give a spectrum with a(1H) 9·1 G, g 2·0002: T. J. Kemp and D. Greatorex, *J.C.S. Faraday I*, 1972, **68**, 121.

Ab initio calculations on the acetyl radical[2] (**15**) show that the value of $a(H_\beta)$ depends on the size of the dihedral angle θ, being *ca.* 13 G when $\theta = 0$, and falling to near zero when θ = 90—180°. In di-t-butylacetaldehyde the carbonyl group eclipses the β-C–H bond,[3] and the corresponding acyl radical (**4**) apparently retains the same conformation (**16**) with $\theta = 0°$ and $a(H_\beta)$ = *ca.* 11 G.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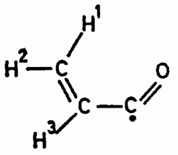
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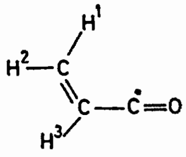
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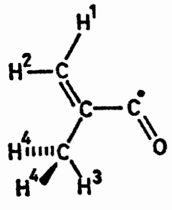
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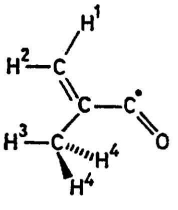
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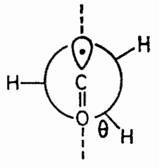
TABLE 2. INDO Calculations of e.s.r. spectra

	$a(H^1)$	$a(H^2)$	$a(H^3)$	$a(H^4)$
(**10**)[a]	0·51	0·00	26·66	—
(**11**)[a]	9·58	1·05	−0·08	—
(**12**)[b]	−9·99	−10·58	4·76	—
(**13**)[c]	0·65	0·18	−0·08	1·93
(**14**)[c]	0·64	0·19	4·23	−0·19

[a] Assuming the same geometry as in acrolein (E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, 1966, **45**, 104). [b] Assuming the same geometry as in acrolein, except that ∠C–C=O = 180°. [c] Assuming the same geometry as in methacrolein (M. Suzuki and K. Kozima, *J. Mol. Spectroscopy*, 1971, **38**, 314).

Simple aldehydes $RCH_2CH{=}O$ are most stable in the conformation where the carbonyl group eclipses the C–R bond,[4] and a more than statistical weighting in favour of a similar conformation (**17**) in the radicals (**1**—**3**) may account for the fact that $a(H_\beta)$ is lower than in the acetyl radical (4·0 G). Radical (**3**) shows non-equivalence of the hydrogens on the β-carbon atom at low temperature.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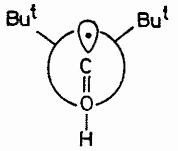
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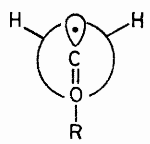
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2,3-Unsaturated aldehydes, because of interaction between the π-systems of the C=C and C=O groups, exist in a planar conformation, the *s-trans* structure being more stable than the *s-cis* by some 13 kJ mol^{-1}.[5] The INDO calculations on the structures (**10**—**12**) suggest that the same *s-trans* conformation persists in the corresponding 2,3-unsaturated acyl radicals (**5**) and (**6**), the high value of $a(H_\beta)$ of *ca.* 20 G arising because of the *trans* coplanar conformation of the β-C–H bond and the σ-orbital containing the unpaired electron.‡ The situation is the same

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‡ At present, the best evidence for the σ-structure of the unsaturated acyl radicals is the correlation with the INDO calculations; we have not as yet been able to measure the value of $a(^{13}C\alpha)$ in natural abundance.

with the cyclopropylacyl radical,[6] which has the same conformation as the parent aldehyde, and, when the β-C–H bond is *trans* to the σ-orbital containing the unpaired electron, the value of $a(H_\beta)$ is 19 G. Radicals (**7**—**9**) illustrate examples of 2-alkylpropenoyl radicals; above −90 °C, the lines are sharp, and hyperfine coupling to both the γ and the δ protons can be observed.

We conclude that the same factors which determine the conformations of aldehydes similarly control the conformations of the corresponding σ-acyl radicals when the bonding electron pair in the sp^2 orbital in the parent is replaced by the unpaired electron in the product.

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[1] Landolt-Börnstein, New Series, II/9b, Springer, Berlin, 1977, pp. 318—322.
[2] H. Veillard and B. Rees, *Chem. Phys. Letters*, 1971, **8**, 267.
[3] G. Karabatsos and N. Hsi, *J. Amer. Chem. Soc.*, 1965, **87**, 2864.
[4] G. Karabatsos and D. J. Fenoglio, *Topics in Stereochem.*, 1970, **5**, 167.
[5] E. A. Cherniak and C. C. Costain, *J. Chem. Phys.*, 1966, **45**, 104.
[6] P. M. Blum, A. G. Davies, and R. Sutcliffe, *J.C.S. Chem. Comm.*, 1979, 217.