

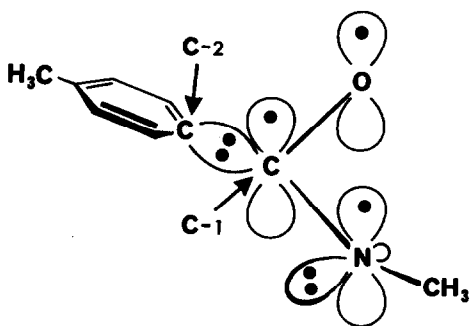
ON THE STRUCTURE OF ACYLAMINYL RADICALS

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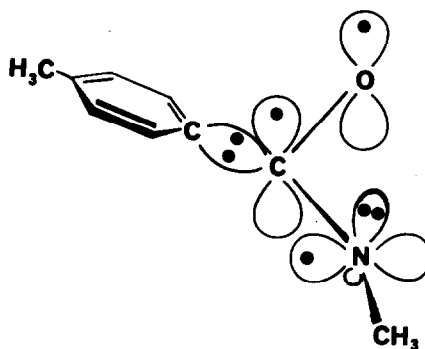
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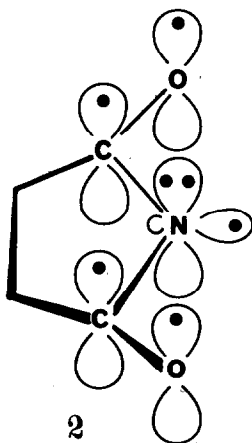
The detailed structure of acylaminyl radicals (such as 1) has been the subject of much debate.¹ The ESR measurements of Danen and Gellert¹, however, resolved much of the controversy surrounding the proposed σ and π structures, in that the unpaired electron was deduced to be localised primarily in a nitrogen orbital of mainly p-character. It is not clear, however, whether the orbital in question conjugates with the carbonyl π -lobes as in 1a, or is located in the nodal plane as in 1b².



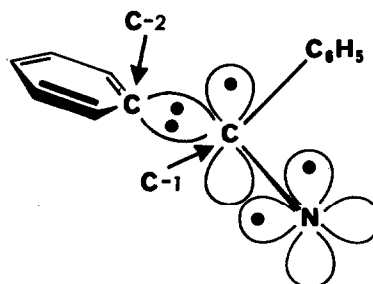
1a



1b



2



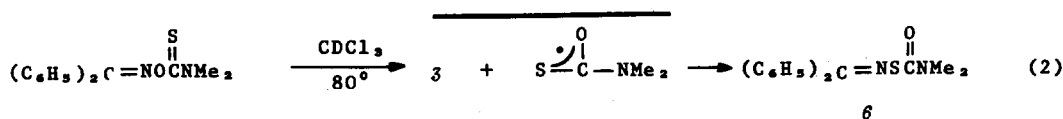
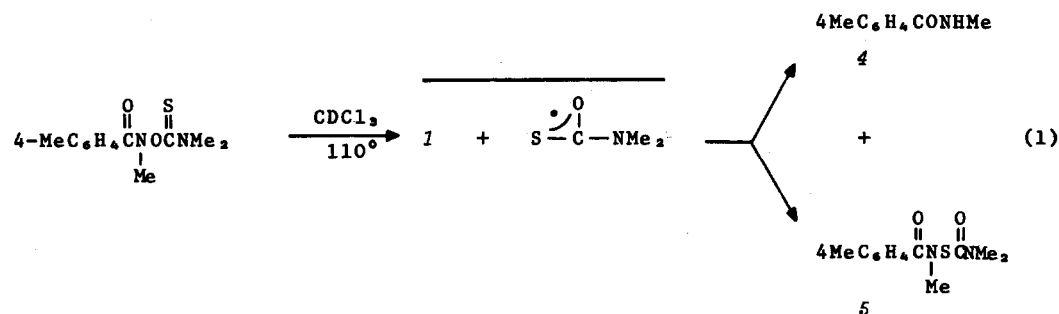
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That the latter merits consideration is shown in particular by the work of Hedaya *et al.*, who concluded³ that the nitrogen non-bonding electrons may preferentially conjugate with the carbonyl function(s) in acylaminyll 1 and succinimidyl radicals 2.

From consideration of interactions⁴ between the nitrogen 2p orbital and the C-1/C-2 sigma bond, 1b should have $|a_{1,C}|$ values for C-1 and C-2 comparable to one another as in 3, in which the unpaired electron can with confidence be assigned⁴⁻⁶ to the nitrogen 2p orbital in the C-N nodal plane. On the other hand, structure 1a does not permit extensive interaction between the unpaired electron and the C-1/C-2 bond, and so this structure should lead (on the basis of a simple spin-polarisation model) to a substantial value of $|a_{1,C}|$ for C-1, but not for C-2.⁷

We wish to report the results of some ¹³C-CIDNP studies (Figure) on the thermal rearrangement of *N*-benzoyl-*N*-methyl-*O*-thiocarbamoylhydroxylamines which not only confirm our earlier proposal⁸ that this reaction proceeds *via* acylaminyll radicals, but which also allow us to distinguish between structures 1a and 1b for such radicals.

The magnitudes of CIDNP effects depend⁹, *inter alia*, on the values of the appropriate hyperfine splitting constants $|a|$. We have therefore compared the polarisations of ¹³C nuclei in the products 4 and 5 derived from radical 1 with those¹⁰ in the product 6 derived from the iminyll radical 3 (equations 1 and 2).



As reported,¹⁰ both C-1 and C-2 in **6** exhibit substantial polarisation. In **4** and **5**, however, although marked polarisation of a number of nuclei including C-1 is observed, no polarisation of the C-2 resonance can be detected (Figure). Preliminary measurements indicate that this is *not* due to a small T_1 value for C-2 in **4** and **5**, and the difference in chemical shift for C-2 in authentic samples of **4** and **5** measured at the reaction temperature rules out the possibility of fortuitous cancellation of E and A effects in the two products.

These results clearly favour structure **1a** for acylaminy radicals, with the unpaired electron in conjugation with the carbonyl group.

We have also carried out INDO calculations on radicals **1** and **3** to compare with the results of the CIDNP experiments. These calculations confirm that while in **3**, $|a_{1s_C}|$ for C-1 and C-2 are of comparable magnitude (*ca.* -1.7 mT and +1.6 mT respectively) the calculated values of a_{1s_C} for the structure **1a** are *ca.* -1.7 mT for C-1 and only *ca.* 0.4 mT for C-2. For conformer **1b** the $|a_{1s_C}|$ values are more comparable (*ca.* -1.2 and 0.9 respectively).

NOTES AND REFERENCES

1. W.C.Danen and R.W.Gellert, *J.Amer.Chem.Soc.*, 94, 6853 (1972) and references therein.
2. The orbital assigned to the lone pair may be regarded as sp^2 or pure p (in which case the nitrogen is taken as sp -hybridised) without appreciably affecting the argument.
3. E.Hedaya, R.L.Hinman, V.Schomaker, S.Theodoropoulos and L.M.Kyle, *J.Amer.Chem.Soc.*, 89, 4875 (1967).
4. J.A.Brivati, K.D.J.Root, M.C.R.Symons and D.J.A.Tinling, *J.Chem.Soc.(A)*, 1942 (1969).
5. D.E.Wood, R.V.Lloyd and D.W.Pratt, *J.Amer.Chem.Soc.*, 92, 4115 (1970).
6. D.Banks and W.Gordy, *Mol.Phys.*, 26, 1555 (1973).
7. There is no compelling evidence for π -delocalisation of the unpaired electron in acylaminyls - see Y.L.Chow and T.C.Joseph, *Chem.Comm.*, 490 (1969).
8. W.B.Ankers, C.Brown, R.F.Hudson and A.J.Lawson, *J.C.S.Chem.Comm.*, 935 (1972).
9. See for example, M.Lehning and H.Fischer, *Z.Naturforsch.*, 25a, 1963 (1970) and J.I.Morris, R.C.Morrison, D.W.Smith and J.F.Garst, *J.Amer.Chem.Soc.*, 94, 2406 (1972).
10. C.Brown, R.F.Hudson and A.J.Lawson, *J.Amer.Chem.Soc.*, 95, 6500 (1973).

FIGURE: ^{13}C FT Spectra of products of reaction shown in equation (1.). Upper trace; spectrum recorded within 5 minutes of placing sample in preheated probe of spectrometer. Lower trace; spectrum recorded 5 minutes later. Each spectrum is the result of 500 accumulated transients.

