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ESR SPECTRA OF N-ALKYL N',N'-DIMETHYLCARBAMOYL AND N-TERT-BUTYL N-CARBOBENZYLOXY AMINYL RADICALS

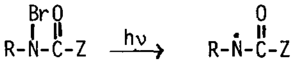
Herman Teeninga and Jan B.F N Engberts*

Department of Organic Chemistry, University of Groningen,
Nijenborgh 16, 9747 AG Groningen, The Netherlands

Summary The first ESR spectral data for the title amidyl radicals are reported They are consistent with π electronic ground states

Recent electron spin resonance (ESR) studies indicate that N-alkylcarboxamidyl radicals ($R\dot{N}C(=O)Z$, Z=alkyl) can be best described as π radicals[1] However, several questions concerning the exact geometry and the extent of unpaired electron delocalization[2] have not yet been settled Therefore it is of considerable interest to study the effect of variation of Z on the ESR parameters of amidyls We report here the first account of the ESR spectra of two structurally related types of amidyls, namely N-alkyl N',N'-dimethylcarbamoyl aminyls ($RNC(=O)NMe_2$, 1a, R=t-Bu, 1b, R=t-Am) and N-tert-butyl N-carbobenzyloxy aminyl (2, $t\text{-Bu}\dot{N}C(=O)OCH_2Ph$) Radicals of type 1 ("ureyls")[3] have previously been invoked as intermediates in the reaction of tert-butylsulfinyl chloride with N-hydroxy-ureas [4] N-Carboalkoxyaminyls have been proposed as intermediates in the addition of N-halocarbamates to alkenes [5]

The amidyls 1a-b and 2 were generated by irradiation of carefully degassed solutions of the parent N-bromo-ureas or carbamate in the cavity of the ESR spectrometer at low



$$R-\overset{Br}{N}-\overset{O}{C}-Z \xrightarrow{h\nu} R-\dot{N}-\overset{O}{C}-Z$$

1a-b, 2

temperatures The observed nitrogen hyperfine splitting (hfs) constants (A_N) and g-values are listed in the Table. Although the observed lines were rather broad, no additional hydrogen hfs (in 1a-b and 2) or nitrogen hfs (in 1a-b) could be resolved The observed A_N and g-values of

Table ESR Spectral Data[a] for the Amidyls $R\dot{N}C(=O)Z$ and the Derived Nitroxides

$R\dot{N}C(=O)Z$					$RN(\dot{O})C(=O)Z$		
R	Z	T (^oC)	A_N (G)	g	T (^oC)	A_N (G)	g
t-Bu	NMe_2	- 53	14 9	2 0047	- 50	11 1[b]	2 0067
		-113	15 1	2 0046			
t-Am	NMe_2	- 82	14 8	2 0047			
t-Bu	OCH_2Ph	- 84	14 0	2 0052	-101	8 2	2 0069
		-114	14 0	2 0051			

[a] Varian E-4 apparatus A Philips SP500WQ lamp, equipped with a lens system, was employed Solvent $CFCl_3$ [b] In ether $A_H^{CH_3}$ = 0 7 G (3H) [7]

1a-b and 2 are characteristic for N-tert-alkyl amidyl radicals and consistent with a π electronic ground state [3b] The somewhat higher g-values for 2 as compared with 1a-b is indicative for spin delocalization onto the second oxygen atom in this radical. The, albeit slightly, different A_N values for 1a-b and 2 reveal that radicals of the type $R\dot{N}C(=O)Z$ are more sensitive to variation of Z than the corresponding sulfonamidyls ($R\dot{N}SO_2Z$) [6]

The Table also shows the relevant ESR parameters[7] for the more persistent nitroxides derived from 1a and 2. They were produced after irradiation of a non-degassed solution of the N-bromo-urea and carbamate during ca 5 sec.

References and Notes

(1) R. Sutcliffe, D. Griller, J Lessard and K.U Ingold, J Am Chem Soc 103, 624 (1981) and references cited therein.
(2) A R. Forrester and H. Irikawa, J Chem Soc., Chem Comm 1981, 253.
(3) (a) Several previous attempts to obtain ESR parameters have been unsuccessful See, for example, G A Helcké and R Fantechi, J Chem Soc , Faraday Trans. II, 1972, 912 and M.C R. Symons, J. Chem. Phys 55, 1493 (1971). (b) However, the powder and single-crystal ESR spectra of the parent radical $H\dot{N}C(=O)NH_2$ have been observed and interpreted in terms of a nitrogen-centered π radical. H Bower, J McRae and M.C R Symons, J Chem Soc. A 1971, 2400
(4) I.P Bleeker and J B.F N Engberts, Recl Trav. Chim Pays-Bas, 98, 120 (1979).
(5) R.S. Neale, Synthesis 1971, 1.
(6) Compare (a) H Teeninga, B Zomer and J B.F N Engberts, J Org Chem 44, 4717 (1979), (b) The same conclusion can be drawn from a comparison of cyclic carbox- and sulfonamidyl radicals, H Teeninga and J B.F.N. Engberts, to be published
(7) Compare R.M Tel and J B F N Engberts, J Org. Chem 42, 3542 (1977).

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