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AMIDO RADICALS II. GENERATION FROM NITROSAMIDES
E.S.R. EVIDENCE FOR A HINDERED ROTATION AROUND A σ BOND

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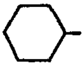
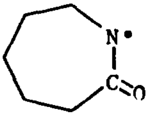
We recently reported (1) E.S.R. evidence supporting a π ground state of the acylamino radical. This radical was obtained by photolysis of 1,4-diacetyl 1,4-dimethyl 2-tetrazene. However tetrazene syntheses are laborious and the preparation of many substituted tetrazenes is out of the question. Therefore, in order to pursue our study, we looked for radical precursors easier to prepare.

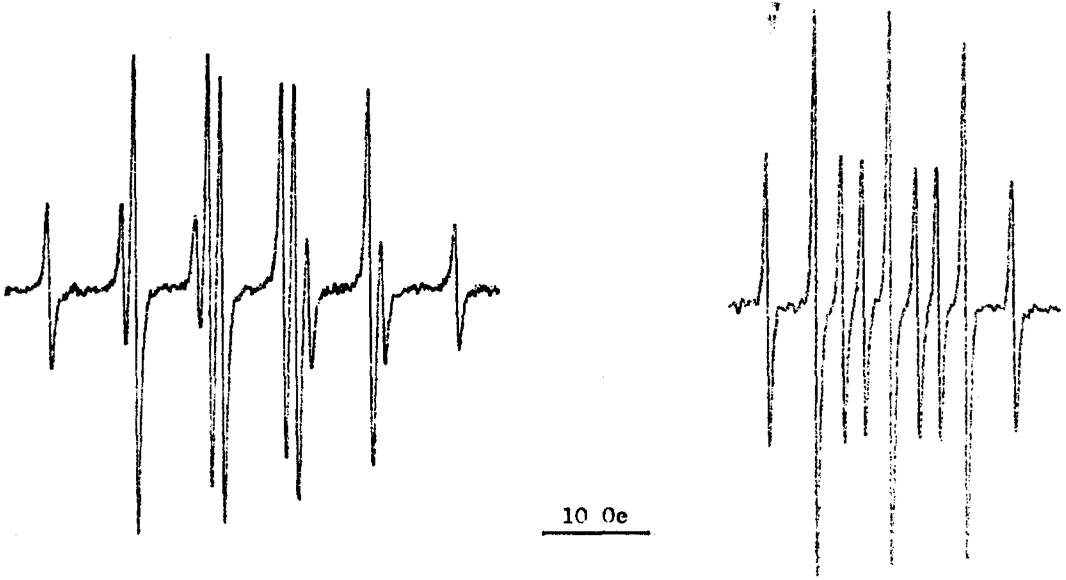
We present here the first direct evidence of amido radical formation from nitrosamides. Indeed "in situ" irradiation (Philips SP 500 W lamp) of N-nitrosamides (2) in solution produces a high concentration of amido radicals, whose hyperfine splittings agree with those of the acylamino radical previously prepared (1), (table).

Table

Features of the spectra recorded in toluene

Radical	θ (°C)	a_N (Oe)	a_H (Oe)	g DPPH	Reference in the text
$CH_3-CO-\dot{N}-Me$	-65	6.9	8.1(3H)	2.0065_5	a
$CH_3-CO-\dot{N}-Et$	-70	6.9	6.1(2H)		b
$CH_3-CO-\dot{N}-iPr$	-80	6.9	2.3(1H)		c
 $-CO-\dot{N}-iPr$	-80	6.9	2.3(1H)		d
$CH_3-CO-\dot{N}-tBu$	-80	7.1	-		e
$CH_3-CO-\dot{N}-Allyl$	-65	6.9	5.2(2H)	2.0066_2	f
$CH_3-CO-\dot{N}-CH_2-\Phi$	-50	6.9	4.4(2H)		g
	-60	7.0	4.4(2H)		h

The spectra recorded (E_3 Varian spectrometer) show a very good resolution (fig. 1) and they can be measured in toluene as well as in n-hexane several minutes after the irradiation has been stopped. The temperature range investigated is very large (-80°C to 0°C) and these observations strongly suggest a high stability of amido radicals which agrees with their π structure.

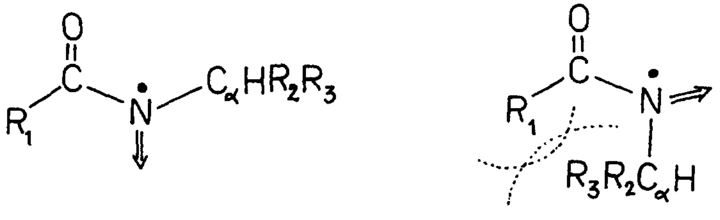


Spectrum of a recorded 20 minutes after irradiation

Spectrum of g recorded 10 minutes after irradiation

Fig. 1

Radicals c and d show a striking similarity in their hyperfine splittings. This strongly suggests that the amido radicals studied here are in a trans conformation, as are the corresponding amides (3) (fig. 2).

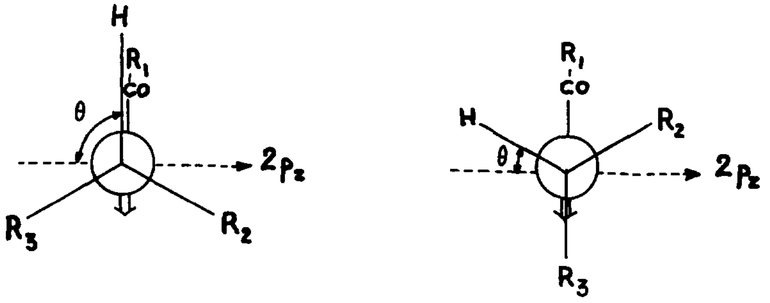


trans cis

Fig. 2

In a trans conformation no steric hindrance exists between R_1 and the C_α substituents. Hence as the size of the R_1 group increases no change occurs in the nature and the populations of the different rotamers around the $N-C_\alpha$ bond ; therefore a_H remains constant as observed. On the other hand, in a cis conformation an increase of steric hindrance would produce a significant modification of a_H.

The variation of a_H value in the series a, b, c, is a salient feature of a hindered rotation around the $N-C_\alpha$ bond. In order to analyse our E.S.R. data it is helpful first, to settle upon the form of the potential energy function for the rotation around this bond. The most plausible form seems to be one analogous to that proposed by Rassat and al. (4) for nitroxides. One of the substituents on the α tetrahedral carbon is in the nodal plane of the π system. Hence for the amido radicals in a trans conformation, we can write three rotamers (fig. 3, s-cis).



only one rotamer
represented
in each case

s-cis

s-trans

Fig. 3

The β couplings in E.S.R. are well known to follow a $\cos^2\theta$ relationship where θ is defined as in fig. 3,

$$a_H = B_2\,\rho_N^\pi\langle\cos^2\theta\rangle$$

B_2 is a constant, ρ_N^π is the electron spin density in the $2p_z$ nitrogen orbital.

The radicals a, b, c, f and g have the same a_N value (table), therefore $\rho_N^\pi \sim$ constant and since $2\,a_H = B_2\,\rho_N^\pi$ for the methyl group (4), we deduce $B_2\,\rho_N^\pi \sim 16.2$ Oe for the series. When the nitrogen substituent is an isopropyl group (c and d), the small a_H hyperfine splitting is in agreement with the stable rotamer where θ is nearly 90°. The average value of $\cos^2 90$ can be deduced from the experiment $\langle\cos^2 90\rangle \sim 2.3/16.2 \sim 0.14$, thus using the Stone and Maki (5) curves we find a potential barrier value of 2.2 kcal/mole. This value is very close to those proposed for aldehydes (6) and nitroxides (3).

Attention must be drawn to the fact that the same conclusions can be reached with a stable conformer where a C_α-R bond is in a s-trans position with regard to the carbonyl. At present we cannot distinguish between these two possibilities.

The photolysis of N-nitrosamides appears to be a very convenient method for the E.S.R. study of amido radicals. The features of all the spectra observed substantiate our claim (1) concerning the π structure of these radicals. We are now working on the question of the conformational aspect at the C_α atom which could be of particular significance in the conformation of peptides.

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