

***N*-Alkyl and *N*-Aryl-carbamoyl Radicals: a New σ -Type Radical**

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Appropriate *N*-alkyl formamides, *ortho* substituted, allow the direct detection, by e.s.r. techniques, of the corresponding aryl carbamoyl σ -radical.

Hydrogen abstraction from alkyl or di-alkyl substituted amides can yield a carbamoyl radical showing the presence of both *trans* and *cis* conformers.¹⁻³ However, no e.s.r. evidence for carbamoyl radicals, generated from *N*-aryl, *N,N*-di-aryl, or *N,N*-aryl,alkyl amides⁴ has been reported. Attempts to

detect directly carbamoyl radicals from formamides, *N*-aryl, and *N*-alkyl formamides, failed because of the rapid decarbonylation process (Scheme 1) leading to aminyl and/or nitroxyl radical species (Table 1).

In *N*-substituted formamides the ring is still nearly co-

Table 1

Amide (1)	Aminyl radical	H.f.s./G ^b	<i>g</i>	Nitroxyl radical	H.f.s./G	<i>g</i>
(1)	—	—	—	PhN(OBu ^t)-O ^{•a}	<i>a</i> _H (<i>m</i>) 0.95 <i>a</i> _H (<i>o,p</i>) 3.0 <i>a</i> _N 14.63	2.0055
(2)	Ph-N-Ph	<i>a</i> _H (4H) 1.50 <i>a</i> _H (4H) 3.60 <i>a</i> _H (2H) 4.20	2.0035	Ph ₂ N-O [•]	<i>a</i> _H (4H) 0.75 <i>a</i> _H (6H) 1.85 <i>a</i> _N 9.65	2.0056
(3)	—	<i>a</i> _H = 8.75	—	PhN(Me)-O [•]	<i>a</i> _H (<i>m</i>) 0.95 <i>a</i> _H (<i>o,p</i>) 2.20 <i>a</i> _H (Me) 9.60 <i>a</i> _N 10.60	2.0056
(4)	Ph-N-Bu ^t	<i>a</i> _H (<i>m</i>) 1.80 <i>a</i> _H (<i>o</i>) 5.60 <i>a</i> _H (<i>p</i>) 6.85 <i>a</i> _N 9.40	2.0031	PhN(Bu ^t)-O [•]	<i>a</i> _H (<i>m</i>) 0.90 <i>a</i> _H (<i>o,p</i>) 1.80 <i>a</i> _N 12.65	2.0055

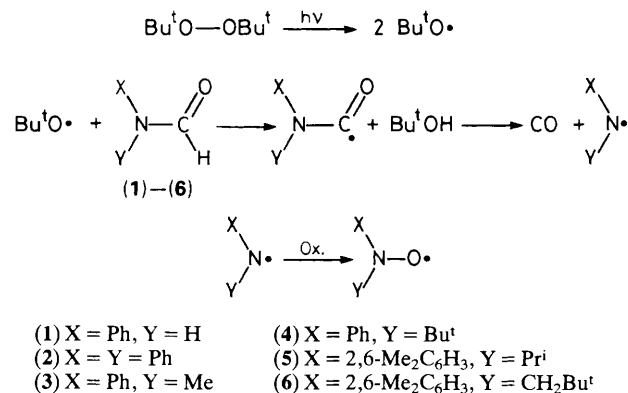
^a This radical is formed in a different way, it seems, depending on the Bu^tOOH impurity, and the mechanism is now under study.

^b *G* = 10⁻⁴ T.

Table 2

Amide (5)	Carbamoyl radical (5')- <i>trans</i>	H.f.s./G	<i>g</i>
		<i>a</i> _H (CH/Pr ⁱ), 3.00 <i>a</i> _H (1 Me/Pr ⁱ), 1.08 <i>a</i> _N , 20.62	2.0019
	(5')- <i>cis</i>	<i>a</i> _H (1H <i>m</i>), 1.42 <i>a</i> _H (1 Me/Ar), 1.14 <i>a</i> _N , 20.62	2.0019
(6)	(6')- <i>trans</i> ^a	<i>a</i> _N , 22.50	2.0017

^a The radical structure is Bu^tCH₂N(C₆H₃Me₂-2,6)-C=O[•].



Scheme 1

planar with the amide plane;⁵ this can explain the high rate of decarbonylation, leading to more persistent radical species, *i.e.* aminyl and nitroxyl radicals,[†] than the corresponding carbamoyl radical.

In *N*-alkyl, *ortho*-substituted formamides, *i.e.* substituted on both the ring and the nitrogen, the ring is definitely perpendicular to the amide plane; this should favour the persistence of carbamoyl radicals. In fact, when *N*-isopropyl-2,6-dimethylformanilide (5) and *N*-neopentyl-2,6-dimethylformanilide (6) were investigated the corresponding carbamoyl radicals were detected (Table 2). With the former substrate, in agreement with the n.m.r. data of the parent molecule, the two possible radical conformers (Figure 1) were identified.

[†] For these radicals there is a stabilizing effect due to the benzene ring.

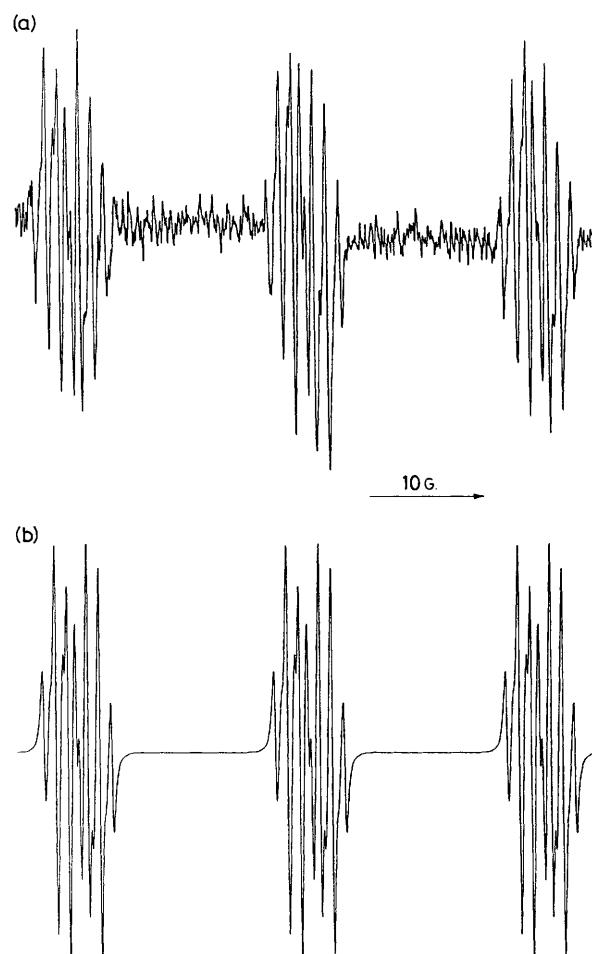
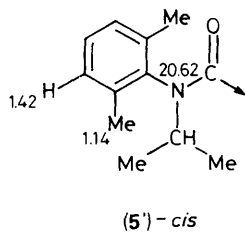
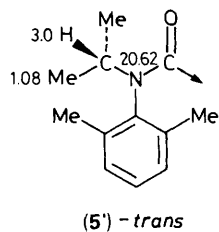


Figure 1. (a) E.s.r. experimental and (b) computer-simulated spectra of radicals (5')-*trans* and (5')-*cis*, simultaneously obtained by hydrogen abstraction from (5) by means of Bu^tO[•], at room temperature in benzene.

Following the W-empirical rule the assignment of the experimental h.f.s. constants to both species (5') was possible, and the low *g*-factor unambiguously identifies these as σ -radicals.



By computer simulation, within experimental error ($\pm 5\%$), the relative concentration of the two radicals was 75:25 (*trans*:*cis*).

For substrate (6) the e.s.r. spectrum shows one radical species: the carbamoyl σ -radical (6'). Only one of the conformers is detectable (95%) and from the n.m.r. data for

the parent molecule it can be attributed to the *trans* conformer.

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