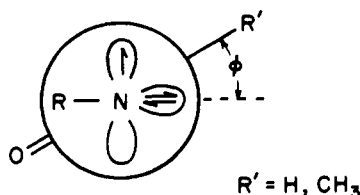


other two formamidyls—just as *N-tert*-butylcarboxamidyls are substantially more “twisted” than other *N*-alkylcarboxamidyls.<sup>4</sup> That is, although both *t*-Bu $\dot{N}$ C(O)H and *t*-Bu $\dot{N}$ C(O)CH<sub>3</sub> have a  $\pi$  electronic structure with the unpaired electron residing in an N 2p orbital perpendicular to the CNC plane, the C(O)H and C(O)CH<sub>3</sub> groups do not lie in this plane.<sup>4</sup> Unfortunately, a detailed calculation of the twist angle,  $\phi$ , from the  $a^H$ (C(O)H) values of the R $\dot{N}$ C(O)H radicals (of the kind made previously from the  $a^{13C}$  values for R $\dot{N}$ C(O)<sup>13</sup>CH<sub>3</sub> radicals)<sup>4</sup> cannot be made. This is because there are no known  $\dot{X}$ C(O)H radicals in which the C(O)H group is perpendicular to the p orbital containing the unpaired electron.<sup>17</sup> However, the similarity in the EPR parameters for pairs of R $\dot{N}$ C(O)H and R $\dot{N}$ C(O)CH<sub>3</sub> radicals implies that  $\phi$  is probably similar for each pair, i.e.,<sup>4</sup> between 22 and 28° for R = *t*-Bu and between 0 and 17° for R = *t*-BuCH<sub>2</sub>.



Finally, we believe it necessary to eliminate specifically some other potential structures for the radicals reported herein.

(1) *N*-Alkylcarbamoyl, RNHC=O. These species, which are  $\sigma$  radicals, have very different EPR parameters to those of the present radicals.<sup>18</sup> They exist as noninterconverting *cis* and *trans* conformers (see accompanying communication).<sup>18</sup> It is worth adding that for none of the three R $\dot{N}$ C(O)H radicals observed was there evidence for more than one radical conformer; to this conformer we assign the *trans* structure 4 by analogy with the *trans* structure of *N*-alkylcarboxamidyls.<sup>4</sup>

(2) Nitroxide, RN(O)C(O)H. Such radicals were produced whenever the sample had not been properly deoxygenated. The EPR parameters for *t*-BuN(O)C(O)H, viz.,  $g = 2.0072$ ,  $a^N = 6.9$  G,  $a^H = 1.4$  G, are in agreement with a previous report.<sup>19</sup>

(3) *N*-Alkylaminyl, RNH. Such radicals could, in principle, be formed by the reaction R $\dot{N}$ C(O)H  $\rightarrow$  RNH + CO. This possibility was eliminated when it was shown that the photolysis of RN(Cl)<sup>13</sup>C(O)H gave radicals exhibiting a <sup>13</sup>C hyperfine splitting (hfs).

(4) 2-Alkyloxazirid-3-yl, RNOCH. Such radicals, which might be formed by a radical cyclization R $\dot{N}$ C(O)H  $\rightarrow$  RNOCH or in

calculations on H $\dot{N}$ C(O)H have supported the  $\pi$  configuration, but SCF calculations on this radical have supported the bent  $\sigma_N$  configuration.<sup>9</sup> INDO calculations on CH<sub>3</sub>N $\dot{C}$ (O)H supported the linear  $\sigma_N$  configuration (6),<sup>7</sup> but recent ab initio calculations suggest a composite of the  $\pi$  and bent  $\sigma_N$  configurations.<sup>10</sup> Baird has concluded on the basis of his detailed ab initio calculations that MO theory at anything but the very highest level cannot make meaningful predictions about radicals of this general type.<sup>11-13</sup>

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a process concerted with chlorine atom loss RN(Cl)C(O)H  $\xrightarrow{h\nu}$  RNOCH + Cl, are unknown. However, they are expected to have <sup>13</sup>C hfs that are very much larger than the 11 G found for the present radicals. In fact, a <sup>13</sup>C hfs of 11 G is in the range expected for a  $\beta$  carbon in a  $\pi$  radical.<sup>20</sup>

In conclusion, we have detected three *N*-alkylformamidyls by EPR spectroscopy and shown that they have a  $\pi$  electronic ground state.

(20) For example,  $a^{13C\beta} = 16.5$  G for 2,2,6,6-tetramethyl-4-oxopiperidin-1-yl<sup>21</sup> and lies in the range 10.4-13.7 G for a series of RCH<sub>2</sub>CH<sub>2</sub> radicals<sup>22</sup> and in the range 6.1-13.0 G for a series of RCH<sub>2</sub>C(*t*-Bu)<sub>2</sub> radicals.<sup>22</sup>

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### *cis*-Alkylcarbamoyl Radicals. The Overlooked Conformer<sup>1</sup>

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It is well-known that *N*-alkylamides exist predominantly or entirely in the *trans* conformation.<sup>3</sup> However, as early as 1964 Laplanche and Rogers<sup>4</sup> showed that *N*-alkylformamides existed in both the *trans* (1) and *cis* (2) conformations, with the *trans* form predominating but with the percentage of the *cis* isomer increasing as the alkyl group became more bulky. One of us



(R.S.) has previously shown by EPR spectroscopy that a wide variety of acyl radicals, RC=O, adopt the same conformation as do their parent aldehydes, RCHO.<sup>5</sup> In addition, it was shown that at temperatures below 183 K the cyclopropylacyl radical existed as a mixture of two conformers of approximately equal stability, the barrier to interconversion of these conformers being ca. 4.2 kcal/mol.<sup>6</sup> Because of the N-C bond of amides has partial double bond character,<sup>3</sup> barriers to internal rotation in amides are very high (ca. 20  $\pm$  5 kcal/mol).<sup>3</sup> This is also true for formamides, the barrier to rotation about the N-C bond in *N*-methylformamide having been estimated to be about 28 kcal/mol.<sup>7</sup> One would therefore expect that in an experiment in which the formyl hydrogen atom was abstracted from an *N*-alkylformamide the 1 isomer should yield the *trans*-alkylcarbamoyl radical (3), while the 2 isomer should yield the *cis* radical (4). Moreover,

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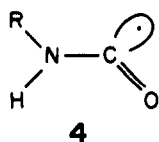
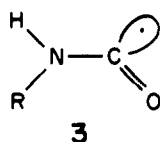
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Table I. EPR Parameters for *trans*- (3) and *cis*-*N*-Alkylcarbamoyl (4) Radicals,<sup>a</sup> Their Percentage Yields,<sup>a</sup> and the Percentage of *Trans* (1) and *Cis* (2) Conformers of the Parent *N*-Alkylformamides

RNHCO	<i>N</i> -alkylcarbamoyl radicals							parent <i>N</i> -alkylformamide	
	conformer	<i>T</i> , K	<i>g</i>	<i>a</i> <sup>N</sup> , G	<i>a</i> <sup>H(NH)</sup> , G	<i>a</i> <sup>other</sup> , G	%	conformer	% <sup>b</sup>
CH <sub>3</sub> NHCO	3 <sup>c</sup>	208	2.0015	24.0	0.9	0.9 (3 H)	93.6	1	92 <sup>d,15</sup>
	4		2.0015	21.2	25.1	<i>d</i>	6.4	2	8 <sup>d,15</sup>
CH <sub>3</sub> CH <sub>2</sub> NHCO	3	219	2.0018	22.4	<i>e</i>	<i>e</i>	84	1	88 <sup>d,15</sup>
	4		2.0017	20.2	25.3	0.7 (2 H)	16	2	12 <sup>d,15</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> NHCO	3	217	2.0018	22.6	<i>e</i>	<i>e</i>	89	1	86 <sup>15</sup>
	4		2.0018	20.5	25.5	0.7 (2 H)	11	2	14 <sup>15</sup>
(CH <sub>3</sub> ) <sub>3</sub> CNHCO	3	214	2.0017	20.6	0.9	0.9 (9 H)	79	1	82, <sup>d</sup> 78 <sup>15,g</sup>
						151.9 (1 C) <sup>f</sup>			
	4		2.0017	18.5	25.7	0.3 (9 H)	21	2	18, <sup>d</sup> 22 <sup>15,g</sup>
					150.5 (1 C) <sup>f</sup>				

<sup>a</sup> These data were obtained in toluene as solvent and were indistinguishable from the results obtained in cyclopropane as solvent. There was no significant change with temperature in the hfs or in the relative concentrations of 3 and 4 with temperature. <sup>b</sup> Note that the precision of these NMR derived population ratios is generally purported to be ca. ±1%. <sup>c</sup> The EPR parameters for this radical are in satisfactory agreement with those reported previously, viz., *g* = 2.00182, *a*<sup>N</sup> = 22.2 G, *a*<sup>H(NH)</sup> = 2.0 G, *a*<sup>H(3 H)</sup> = 1.0 G; <sup>d</sup> *g* = 2.0017, *a*<sup>N</sup> = 23.78 G, *a*<sup>H(3 H)</sup> = 1.02 G.<sup>10</sup> <sup>e</sup> Not resolved. <sup>f</sup> An incompletely resolved complex multiplet was observed with hfs in the range 0.9–1.2 G. <sup>g</sup> Derived from measurements on (CH<sub>3</sub>)<sub>3</sub>CNH<sup>13</sup>CO. <sup>h</sup> Reference 14 gives relative concentrations of 1 and 2 of 70 and 30, respectively, for this formamide. These values must be in error.



these isomeric radicals, which will have a  $\sigma$  electronic structure, should not interconvert (on the EPR time scale) since the electronic effects which produce high barriers in amides<sup>3</sup> will not be (appreciably) changed in these radicals. In addition, the relative yields of 3 and 4 should not differ significantly from the relative concentrations of 1 and 2 in the starting *N*-alkylformamide.

On searching the literature, we were surprised to find that the only *N*-alkylcarbamoyl radical for which an EPR spectrum has been reported is CH<sub>3</sub>NHCO and that although this radical has been observed by three separate groups of workers<sup>8-10</sup> only the *trans* isomer had been detected. We have therefore photolyzed solutions containing four different *N*-alkylformamides and di-*tert*-butyl peroxide in toluene and cyclopropane as solvents, directly in the cavity of a Varian E-104 EPR spectrometer. We were not surprised to see two *N*-alkylcarbamoyl radicals from each *N*-alkylformamide.<sup>11</sup> No other radicals were formed, i.e., there was no abstraction of the amide hydrogen<sup>12</sup> nor was there abstraction from the R group.

The EPR parameters for these carbamoyl radicals and their relative concentrations<sup>13</sup> in toluene are summarized in Table I. Within experimental error the hyperfine splittings (h.f.s.) for the individual radicals and the relative concentrations of each pair of carbamoyl radicals did not vary over the temperature range studied (ca. 210–300 K). The percentage yields of the *trans* and *cis* radical isomers are in excellent agreement with the NMR derived percentage concentrations of their individual parents as reported in the literature.<sup>4,14,15</sup> Since the *trans* and *cis* radicals are sterically nonhindered and are of identical molecular weight, they will decay (i.e., undergo their bimolecular self-reactions) at the same rates.<sup>16</sup> Their relative concentrations will therefore be determined only by their relative rates of formation. Since their relative concentration are equal to the relative concentrations of

their individual parents, the rate constants for the reactions



must be equal.

Examination of the EPR data shows that within experimental error both radical conformers have the same *g* values. For the minor radical the value of *a*<sup>H(NH)</sup> is always much larger than the value for the major radical. By analogy with other  $\sigma$  radicals (such as, for example, vinyl<sup>17</sup>) this serves to confirm that the minor radical has the *cis* structure, 4 with the NH hydrogen located *trans* to the orbital containing the unpaired electron. The value of *a*<sup>N</sup> is about 10% smaller for 4 than for 3 which we considered might be due to differences in the hybridization or spin density<sup>18</sup> of the acyl carbons. With the hope of throwing some light on the origin of this difference in *a*<sup>N</sup> values we therefore measured *a*<sup>13C</sup> for the two isomeric radicals derived from (CH<sub>3</sub>)<sub>3</sub>CNH<sup>13</sup>CHO (using 90% <sup>13</sup>C enriched material). However, the <sup>13</sup>C hfs obtained were within 1% of each other (see Table I) which implies that any changes in hybridization and spin density are either very small or mutually compensating with respect to *a*<sup>13C</sup>.

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(18) Structure 4 might be expected to have a lower spin density on the acyl carbon because of the increased delocalization of the unpaired electron on to the NH hydrogen.

## Stereospecific Reactions of Dichloroketene with Vinyl Sulfoxides: A New Type of Polar Cycloaddition

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The vinyl sulfide and sulfoxide functionalities have assumed an increasingly important role in synthetic chemistry.<sup>1</sup> During the course of our investigations on new methods for synthesizing  $\alpha$ -methylene- $\gamma$ -butyrolactone natural products, we sought a process

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