3 was isolated. No conditions were found which resulted in exclusive formation of symmetric dimer **2**. The selectivity for asymmetric dimer formation resulting from use of the tetramethylammonium cation is evident on comparison of experiments 2 and 3. Replacement of lithium chloride by tetramethylammonium chloride resulted in a change in dimer formation from a ratio of symmetric (**2**) to asymmetric (**3**) of 6:1 (Li^+, experiment 2) to 1:2 (Me_4N^+, experiment 3). Under the latter conditions, trimer **4**[12] was produced in addition to the dimers.

Use of less than stoichiometric quantities of palladium salt resulted in diminished yields (experiments 8, 9, 12). It is noteworthy that 1,3-dimethyl-2,4(1*H*,3*H*)-pyrimidinedione[13] underwent dimerization in the presence of palladium acetate (experiments 11, 12), essentially as effectively as the corresponding mercuric derivative (**1**).

The results of this study underscore the striking selectivity of transition-metal-catalyzed reactions and emphasize the need to develop a deeper understanding of factors which determine selection among permissible reaction pathways.

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[12] Mp >350 °C. Anal. Found for $C_{18}H_{20}N_6O_6$: C, 51.9; H, 5.01; N, 20.1. ^1H NMR ($CDCl_3$) δ 3.26, 3.29, 3.33, 3.53, 3.63 (NMes), 7.08, 7.59 (pyrimidine Hs).

[13] Yamauchi, K.; Kinoshita, M. *J. Chem. Soc., Chem. Commun.* **1973**, 391.

N-Alkylformamidyl Radicals. Identification and Electronic Structure[1]

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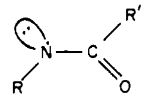
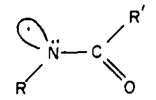
We[3,4] and others[5] have recently shown by EPR spectroscopy that *N*-alkylcarboxamidyl radicals, RNC(O)R′, have the π electronic configuration (**1**) in their ground state rather than the bent (**2**) or linear (**3**) σ_N configurations, thus ending many years of somewhat inconclusive arguments based on the results of theoretical calculations.[6] For the related *N*-alkylformamidyl radicals, $R\dot{N}C(O)H$, there is no experimental information, though Danen and Neugebauer in their 1975 review[14] note that the EPR spectrum of such a radical "would be very informative by virtue of the large coupling constant a^H(CHO) anticipated for a σ_N configuration (i.e., **5**). . .but attempts to generate $(CH_3)_3C\dot{N}C(O)H$ either in solution or in adamantane matrix have not been fruitful". The EPR experience we had gained with $R\dot{N}C(O)R'$ radicals gave us confidence that we would be able to observe $R\dot{N}C(O)H$ radicals provided R was sufficiently bulky. Such proved to be the case, and our results provide unequivocal proof that $R\dot{N}C(O)H$ radicals have the same electronic ground state as $R\dot{N}C(O)R'$ radicals, i.e., the π configuration, **4**.



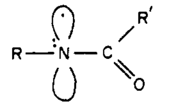
1 R,R′ = alkyl

4 R = alkyl, R′ = H



2 R,R′ = alkyl

5 R = alkyl, R′ = H



3 R,R′ = alkyl

6 R = alkyl, R′ = H

N-Alkylformamidyls having R = *t*-$BuCH_2$, $(t\text{-}Bu)_2CH$, and *t*-Bu were observed[15] upon photolysis under oxygen-free conditions of their parent *N*-chloroformamides in cyclopropane solvent in the cavity of a Varian E-104 EPR spectrometer.[3,4,16] The identity of these radicals and the conclusion that they have the π electronic ground state, **4**, is established by comparison of their EPR parameters with those of the corresponding $R\dot{N}C(O)CH_3$ radicals as measured at or near the same temperatures[3,4] (see Table I). Because the temperature ranges over which the formamidyls could be detected were somewhat limited, we are unable to apply the detailed arguments about structure that were employed previously.[3,4] Nevertheless, the excellent agreement between the *g* and a^N values for each pair of radicals, and between the magnitudes of $a^{H}\beta$ for R = *t*-$BuCH_2$ and $(t\text{-}Bu)_2CH$, establishes that $R\dot{N}C(O)H$ and $R\dot{N}C(O)R'$ radicals have the same electronic structure, i.e., **4** and **1**, respectively. Furthermore, the relatively low *g* value plus the enhanced values of a^N and a^H(CHO) for $t\text{-}Bu\dot{N}C(O)H$ implies that this radical is substantially more "twisted" than the

Table I. EPR Parameters for Some RNC(O)H and Related $R\dot{N}C(O)CH_3$ Radicals

radical	*T*, K	*g*	a^N, G	$a^{H}\beta$(R), G	a^H(CHO), G	a^D(CDO),[a] G	a^{13C}(CHO),[b] G	$a^{13C}(CH_3)$,[c] G
t-$BuCH_2NC(O)H$	158	2.0054	14.8	40.7	10.3	1.4	11.0	
	188	2.0054	14.7	39.3	d	1.4		
t-$BuCH_2\dot{N}C(O)CH_3$[e,f]	161	2.0051	15.1	40.3				2.4
	190		15.0	39.2				
$(t\text{-}Bu)_2CH\dot{N}C(O)H$	159	2.0056	14.4	12.4	7.4	*g*, *h*	11.4[g,i]	
	199	2.0056	14.4	11.7	7.5	*g*, *h*		
	228	2.0056	14.3	11.3		*g*, *h*		
$(t\text{-}Bu)_2CH\dot{N}C(O)CH_3$[e]	153	2.0056	14.7	12.6				*j*
	193		*i*	12.3				
	233		*i*	12.1				
t-$Bu\dot{N}C(OH)$	194	2.0044	16.1		21.5	3.4	k	
t-$Bu\dot{N}C(O)CH_3$[e,l]	173	2.0044	15.8					4.6

[a] By photolysis of RN(Cl)C(O)D. [b] By photolysis of $RN(Cl)^{13}C(O)H$. [c] By photolysis of $RN(Cl)^{13}C(O)CH_3$. [d] Not measured; only *t*-$BuCH_2NC(O)D$ examined at this temperature. [e] Reference 4. [f] The other *t*-$BuCH_2\dot{N}C(O)R'$ radicals have similar parameters:[4] e.g., R′ = Et at 161 K, $g = 2.0053$, $a^N = 14.9$G, $a^{H}\beta = 40.3$ G; R′ = *t*-Bu at 153 K, g = 2.0053, $a^N = 15.2$ G, $a^{H}\beta = 40.9$ G. [g] Not fully resolved. [h] Line width, $\Delta H_{pp} = 3.4$ G. [i] Obtained from total spectral width. [j] Not measured. [k] Spectral intensity too poor to allow analysis. [l] The other *t*-$Bu\dot{N}C(O)R'$ radicals have similar parameters: e.g., R′ = Et at 169 K, $g = 2.0045$, $a^N = 15.6$ G R′ = *t*-Bu at 143 K, $g = 2.0049$, $a^N =$ 15.7 G.

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[1] Issued as N.R.C.C. No. 19841.

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[3] Lessard, J.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 3262–3264.

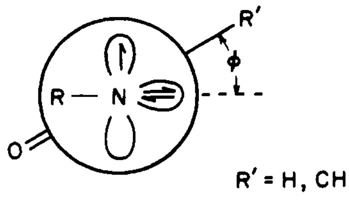
[4] Sutcliffe, R.; Griller, D.; Lessard, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 624–628.

[5] Danen, W. C.; Gellert, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 3264–3265.

[6] INDO,[7] ab initio,[8] and multiconfiguration (MC)–SCF MINDO/3[9]

0002-7863/81/1503-7685$01.25/0

other two formamidyls—just as *N-tert*-butylcarboxamidyls are substantially more "twisted" than other *N*-alkylcarboxamidyls.[4] That is, although both $t\text{-}\mathrm{Bu\dot{N}C(O)H}$ and $t\text{-}\mathrm{Bu\dot{N}C(O)CH_3}$ have a π electronic structure with the unpaired electron residing in an N 2p orbital perpendicular to the CNC plane, the C(O)H and $\mathrm{C(O)CH_3}$ groups do not lie in this plane.[4] Unfortunately, a detailed calculation of the twist angle, ϕ, from the $a^{\mathrm{H}}(\mathrm{C(O)H})$ values of the $\mathrm{R\dot{N}C(O)H}$ radicals (of the kind made previously from the $a^{^{13}\mathrm{C}}$ values for $\mathrm{R\dot{N}C(O)^{13}CH_3}$ radicals)[4] cannot be made. This is because there are no known $\mathrm{\dot{X}C(O)H}$ radicals in which the C(O)H group is perpendicular to the p orbital containing the unpaired electron.[17] However, the similarity in the EPR parameters for pairs of $\mathrm{R\dot{N}C(O)H}$ and $\mathrm{R\dot{N}C(O)CH_3}$ radicals implies that ϕ is probably similar for each pair, i.e.,[4] between 22 and 28° for R = t-Bu and between 0 and 17° for R = $t\text{-}\mathrm{BuCH_2}$.



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

(1) ***N*-Alkylcarbamoyl, $\mathbf{RNH\dot{C}{=}O}$.** These species, which are σ radicals, have very different EPR parameters to those of the present radicals.[18] They exist as noninterconverting cis and trans conformers (see accompanying communication).[18] It is worth adding that for none of the three $\mathrm{R\dot{N}C(O)H}$ 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.[4]

(2) **Nitroxide, $\mathbf{RN(\dot{O})C(O)H}$.** Such radicals were produced whenever the sample had not been properly deoxygenated. The EPR parameters for $t\text{-}\mathrm{BuN(\dot{O})C(O)H}$, viz., $g = 2.0072$, $a^{\mathrm{N}} = 6.9$ G, $a^{\mathrm{H}} = 1.4$ G, are in agreement with a previous report.[19]

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

(4) **2-Alkyloxazirid-3-yl, $\mathbf{R\overline{NO\dot{C}}H}$.** Such radicals, which might be formed by a radical cyclization $\mathrm{R\dot{N}C(O)H \rightarrow R\overline{NO\dot{C}}H}$ or in a process concerted with chlorine atom loss $\mathrm{RN(Cl)C(O)H \xrightarrow{h\nu} R\overline{NO\dot{C}}H + \dot{Cl}}$, are unknown. However, they are expected to have $^{13}\mathrm{C}$ hfs that are very much larger than the 11 G found for the present radicals. In fact, a $^{13}\mathrm{C}$ hfs of 11 G is in the range expected for a β carbon in a π radical.[20]

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

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calculations on $\mathrm{H\dot{N}C(O)H}$ have supported the π configuration, but SCF calculations on this radical have supported the bent σ_{N} configuration.[9] INDO calculations on $\mathrm{CH_3\dot{N}C(O)H}$ supported the linear σ_{N} configuration (**6**),[7] but recent ab initio calculations suggest a composite of the π and bent σ_{N} configurations.[10] 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.[11-13]

(7) Koenig, T.; Hoobler, J. A.; Klopfenstein, C. E.; Hedden, G.; Sunderman, F.; Russell, B. R. *J. Am. Chem. Soc.* **1974**, *96*, 4573-4577.

(8) Baird, N. C.; Kathpal, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7532-7535.

(9) Kikuchi, O. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3149-3153.

(10) Teeninga, H.; Nieuwpoort, W. C.; Engberts, J. B. F. N. *Z. Naturforsch.* **1981**, *36B*, 279-281.

(11) Baird, N. C.; Gupta, R. R.; Taylor, K. F. *J. Am. Chem. Soc.* **1979**, *101*, 4531-4533.

(12) Baird, N. C.; Taylor, K. F. *Can. J. Chem.* **1980**, *58*, 733-738.

(13) Baird, N. C., private communication.

(14) Danen, W. C.; Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 783-789.

(15) The radicals with R = Me, Et, and *n*-Bu could not be positively identified. They are presumably more reactive.

(16) Danen, W. C.; Gellert, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 6853-6854.

(17) Even $(t\text{-}\mathrm{Bu})_2\mathrm{\dot{C}C(O)H}$ is planar. See: Malatesta, V.; Forrest, D.; Ingold, K. U. *J. Phys. Chem.* **1978**, *82*, 2370-2373.

(18) Sutcliffe, R.; Ingold, K. U. *J. Am. Chem. Soc.*, following paper in this issue.

(19) Hartgerink, J. W.; Engberts, J. B. F. N.; de Boer, Th. J. *Tetrahedron Lett.* **1971**, 2709-2712.

(20) For example, $a^{^{13}\mathrm{C}}\beta = 16.5$ G for 2,2,6,6-tetramethyl-4-oxopiperidin-1-yl[21] and lies in the range 10.4-13.7 G for a series of $\mathrm{RCH_2\dot{C}H_2}$ radicals[22] and in the range 6.1-13.0 G for a series of $\mathrm{RCH_2\dot{C}}(t\text{-}\mathrm{Bu})_2$ radicals.[22]

(21) Sholle, V. D.; Rozantsev, E. G.; Prokofev, A. I.; Solodovnikov, S. P. *Izv. Akad. Nauk. S.S.S.R., Ser. Khim.* **1967**, 2628-2631.

(22) Scaiano, J. C.; Ingold, K. U. *J. Phys. Chem.* **1976**, *80*, 275-278.

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cis-Alkylcarbamoyl Radicals. The Overlooked Conformer[1]

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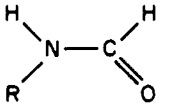
It is well-known that *N*-alkylamides exist predominantly or entirely in the trans conformation.[3] However, as early as 1964 Laplanche and Rogers[4] showed that *N*-alkylformamides existed in both the trans (**1**) and cis (**2**) conformations, with the trans form predominating but with the percentage 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, $\mathrm{R\dot{C}{=}O}$, adopt the same conformation as do their parent aldehydes, RCHO.[5] 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.[6] Because of the N–C bond of amides has partial double bond character,[3] barriers to internal rotation in amides are very high (ca. 20 ± 5 kcal/mol).[3] 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.[7] 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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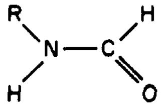
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(1) Issued as N.R.C.C. No. 19842.

(2) N.R.C.C. Research Associate, 1979-1981.

(3) For reviews, see: Stewart, W. E.; Sidall, T. H., III. *Chem. Rev.* **1970**, *70*, 517-551. Robin, M. B.; Bovey, F. A.; Brasch, H. In "The Chemistry of Amides"; Zabicky, J., Ed.; Interscience: New York, 1970; Chapter 1.

(4) LaPlanche, L. A.; Rogers, M. T. *J. Am. Chem. Soc.* **1964**, *86*, 337-341.

(5) Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 819-824.

(6) Blum, P. M.; Davies, A. G.; Sutcliffe, R. *J. Chem. Soc., Chem. Commun.* **1979**, 217-218.

(7) Suzuki, I. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 540-551.