Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 40. Intramolecular Reactions of Some *N*-Alkylcarboxamidyl Radicals[1]

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Abstract: An extensive search for an amidyl radical that would undergo a rearrangement at a rate that could be measured by kinetic EPR spectroscopy, and could therefore serve as a free-radical clock, is described. Approximate or limiting rate constants at specific temperatures were obtained for some intramolecular H-atom abstractions and cyclizations onto C=C double bonds involving acyclic amidyl radicals and for some ring-opening reactions of *N*-cycloalkylamidyl radicals. These kinetic data have been combined with estimated Arrhenius preexponential factors to yield approximate activation energies. Rate constants at 300 K estimated for H abstractions via six-center cyclic transition states are 1×10^5 s^{-1} and 4×10^4 s^{-1} for abstraction from a methyl group in the alkyl and acyl moieties, respectively, and 5×10^6 s^{-1} for abstraction from an allylic position in the acyl group. For exo cyclizations, rate constants at 300 K are estimated to be $\geq 1 \times 10^7$ s^{-1} and 1×10^6 s^{-1} for the formation of five- and six-membered rings involving the acyl moiety but only 5×10^4 s^{-1} for the formation of a five-membered ring involving the alkyl moiety. Rate constants for the ring openings of *N*-cyclopropyl-, *N*-cyclobutyl-, and *N*-cyclopentylamidyl radicals are estimated to be $\gg 2 \times 10^8$ s^{-1}, $>4 \times 10^8$ s^{-1}, and $<8 \times 10^4$ s^{-1}, respectively, at 300 K.

Radicals that undergo irreversible unimolecular reactions at known rates have been christened "free-radical clocks".[3] Such clocks are widely used to determine the rate at which radicals of a specific class undergo intermolecular reactions with various substrates. The utility of this approach is governed by the existence of suitably extensive horlogeries[3] of "calibrated" clocks for all the different classes of free radicals commonly encountered in organic chemistry. A severe deficiency in this regard exists in the area of nitrogen-centered free-radical chemistry since there would appear to be only two nitrogen-centered radical clocks,[3] viz., a dialkylaminyl clock[4] and a dialkylketiminyl clock.[5] In the present paper we describe a protracted search for an *N*-alkylcarboxamidyl (amidyl) radical, RNCOR′, that would undergo a rearrangement[6] that could be both identified by EPR spectroscopy and for which the rate could be measured by the technique of kinetic EPR spectroscopy.[4,7]

Qualitative studies reported in the literature[8] have shown that amidyl radicals are reasonably reactive in intramolecular hydrogen atom abstractions[8-21] and in intramolecular additions to C=C double bonds.[8,22-26] The latter reaction is preferred,[8,25,26] as may[27] or may not[28] be the case for the intermolecular analogues of these two reactions. It has also been shown that an *N*-cyclopropylcarboxamidyl radical undergoes a facile opening of the cyclopropyl ring.[29] Our search for an amidyl radical clock therefore encompassed intramolecular H-atom abstractions, intramolecular cyclizations onto C=C double bonds, and the ring opening of *N*-cycloalkylamidyl radicals.

Experimental Section

Materials. Two of the amides used in this work were gifts from Professor J. Lessard. The remainder were prepared by standard procedures from the corresponding acid and amine.[24] They were converted to the corresponding *N*-chloro amides in the usual way,[1,26] and the latter were carefully purified by high-vacuum distillation or by thin-layer chromatography since the compounds must be water white if good EPR signals are to be obtained.[1]

Procedure. Radicals were generated directly in the cavity of a Varian E-104 EPR spectrometer by UV photolysis of carefully deoxygenated solutions of the chloro amides in cyclopropane. The EPR spectral parameters of the radicals observed were obtained by using an ^{1}H NMR field marker and microwave frequency counter, with correction for the placement of the field marker being made via the tetracene radical cation.[30]

Results and Discussion

Intramolecular Hydrogen Atom Abstractions. Suitably constituted acyclic amidyl radicals can undergo intramolecular hydrogen atom abstraction via the usual six-membered cyclic

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(2) NRCC Research Associate, 1979–1981.
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(10) Barton, D. H. R.; Beckwith, A. L. J.; Goosen, A. *J. Chem. Soc.* **1965**, 181–190.
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(19) Johnson, R. A.; Greene, F. D. *J. Org. Chem.* **1975**, *40*, 2186–2192, 2192–2196.
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(23) Flesia, E.; Croatto, A.; Tordo, P.; Surzur, J. M. *Tetrahedron Lett.* **1972**, 535–538.
(24) Kuehne, M. E.; Horne, D. A. *J. Org. Chem.* **1975**, *40*, 1287–1292.
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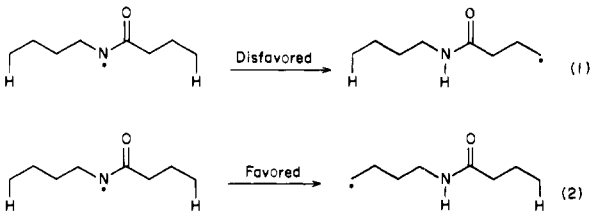
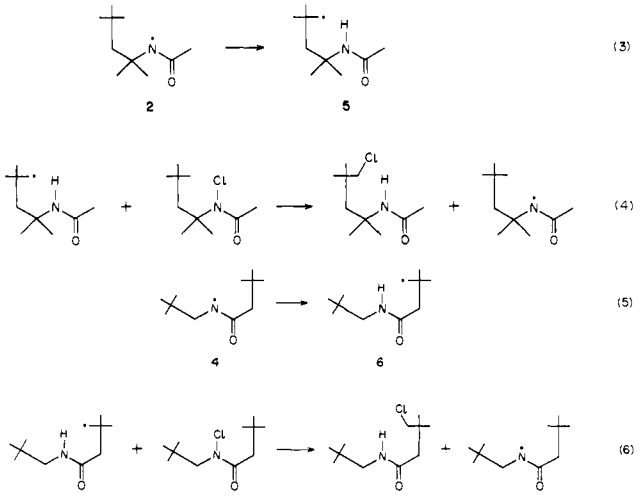
transition state.[6] There is a preference for the abstraction of a δ-H from the alkyl chain rather than a γ-H from the acyl chain.[14-17,21] This preference can be attributed to the fact that



the alkyl side chain can rotate freely to gain a near colinearity of the semioccupied N $2p_z$ orbital and a C–H bond at the δ carbon, thereby achieving maximum orbital overlap.[14,21,31] In contrast, even to approach a coplanar conformation of the γ-C–H bond of the acyl side chain and the N $2p_z$ orbital leaves the γ C and the N rather far apart for effecting a hydrogen atom transfer.[21,31] However, it should be noted that abstraction from the acyl side chain can occur, particularly with *N-tert*-butyl amidyl radicals.[12,19,21] This facilitation, relative to other intermolecular reactions, of the intramolecular H abstraction from the acyl chain has been attributed[21] to the twisting of the R′CO group out of the CNC plane that is induced by the severe steric repulsion between the *N-tert*-butyl group and the carbonyl oxygen. This distortion of the preferred amidyl configuration, which has since been confirmed by EPR spectroscopy,[32] helps the amidyl radical to attain a transition-state geometry that would allow abstraction of the acyl group's γ-H. No doubt a factor that is equally or more important in the promotion of this intramolecular reaction is the reduced rate of the bimolecular reactions of *N-tert*-butyl amidyl radicals relative to their less hindered analogues.[1]

In view of the facts outlined above, we chose for examination the four chloro amides that, on photolysis at low temperatures, yielded EPR spectra of the amidyl radicals identified as **1–4** in Table I. The EPR spectra of all four amidyls were relatively intense at the temperatures at which their parameters were recorded (viz. 173–203 K, see Table I). On raising the temperature to ca. 220 K, the intensities of all the amidyl radicals' spectra diminished rapidly. This was due to depletion of the chloro amide, presumably by a free-radical chain process involving intramolecular hydrogen abstraction; that is, for example, either eq 3 and 4 or eq 5 and 6. The poor quality of the spectra of **1–3** and **4**



at ca. 223 K contrasts with the ready observation[1] of the spectra of other *N-tert*-butyl and *N*-neopentyl amidyl radicals at 298 and 273 K, respectively.

(31) An alternative explanation that invoked a geometry in which the alkyl group on nitrogen and that on the carbonyl group had a cis configuration[15] can be ruled out since it now appears to be firmly established that amidyl radicals have a trans configuration.[32]

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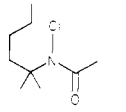
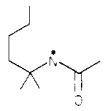
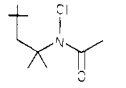
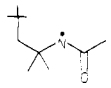
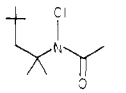
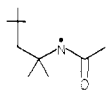
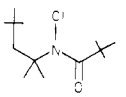
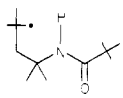
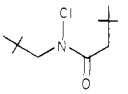
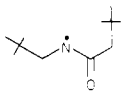
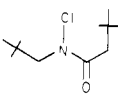
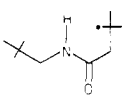
Table I. Intramolecular H-Atom Abstractions: Structure and EPR Parameters of Radicals Observed during Photolysis of Some Appropriate Chloro Amides in Cyclopropane[a]

chloro amide	radical	T, K	g	a^N	a^H
	 1	203	2.0045	15.3	*b*
	 2	173	*c*	15.0	
	 3	193	*c*	15.5	
	 5	233	2.0025		22.0 (2)
	 4	193	*c*	15.0	38.5 (2) 1.9 (2)
	 6	243	*c*		22.0 (2)

[a] Hyperfine splittings (hfs) are given in gauss; the numbers in parentheses in the a^H column refer to the number of equivalent hydrogen atoms. [b] Additional hfs was observed but could not be fully resolved. [c] Not measured.

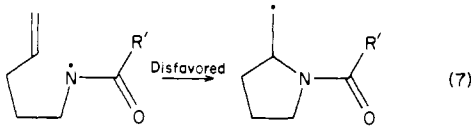
At temperatures of 213–243 K where the chloro amide is being rapidly consumed and the amidyl radical's EPR spectrum is either not observable or very weak, the chloro amide precursors of **1** and **3** did not yield an identifiable alkyl radical. However, the precursors of **2** and **4** did give EPR spectra that, though they could be observed only briefly, could be unequivocally identified as arising from primary alkyl radicals to which we assign structures **5** and **6**, respectively (see Table I). Structure **6** is based on the assumption that abstraction from the acyl chain via a six-membered cyclic transition state will be favored over abstraction from the alkyl chain via a five-membered cyclic transition state. Our observation of alkyl radicals from only two of the four systems studied suggests that the detection of an alkyl under conditions in which the chloro amide is being rapidly consumed is largely a matter of luck.

In order to calculate accurate values for the rate constants for these intramolecular H-atom abstractions, it would be necessary to be able to observe the unrearranged amidyl radicals and the rearranged alkyl radicals simultaneously and to measure their absolute concentration under steady-state conditions.[3] The occurrence of a chloro amide consuming chain reaction renders this procedure impossible. However, a rough estimate of the rearrangement rate constant can, nevertheless, be obtained as follows. The concentration of **4** at $T \leq$ ca. 223 K was ca. 5×10^{-7} M. Like other *N*-neopentyl amidyl radicals,[1] **4** decays with second-order kinetics at such temperatures and with a rate constant for its bimolecular self-reaction, $2k_t^4$, of ca. 10^9 M^{-1} s^{-1}. At 243 K, the intramolecular H-atom abstraction competes successfully with all other processes by which **4** is destroyed since only **6** could be observed. Therefore, at 243 K, $k_5[\mathbf{4}] > 2k_t^4[\mathbf{4}]^2$, i.e., $k_5 > 500$ s^{-1}, while at 223 K, $k_5[\mathbf{4}] < 2k_t^4[\mathbf{4}]^2$, i.e., $k_5 < 500$ s^{-1}. A value for k_5 of 500 s^{-1} at 233 K would appear reasonable. For the **2** → **5** rearrangement, the much smaller value[1] for $2k_t^2$ is compensated by a higher steady-state concentration of **2** at low tem-

peratures. A value for k_3 of ca. 500 s^{-1} at 213 K can be estimated.

These values for k_3 and k_5 at these temperatures are quite consistent with our rate constant, 6.4×10^3 M^{-1} s^{-1}, obtained at 301 K for the intermolecular H-atom abstraction from cyclohexane by the EtNCOEt radical.[1] That is, the transition state for reaction 3 requires the freezing-out of four internal rotations. For reaction 5, the rigidity of the amidyl moiety reduces by one the number of internal rotations that must be frozen in the transition state. That is, the Arrhenius preexponential factors for these reactions are expected to be $A_3 \approx 10^{10.6}$ s^{-1} and $A_5 \approx 10^{11.2}$ s^{-1}. Combining these A factors with the k_3 and k_5 values given above yields $E_3 \approx 7.7$ kcal/mol, $E_5 \approx 9.1$ kcal/mol, and $k_3 \approx 1 \times 10^5$ s^{-1} and $k_5 \approx 4 \times 10^4$ s^{-1} at 300 K. The numerical values of rate constants for intramolecular reactions are generally somewhat larger than the numerical value of the rate constants for analogous intermolecular reactions,[6] a phenomenon that reflects the relatively large "effective" molarity in the intramolecular process.

Cyclizations onto C=C Double Bonds. Suitably constituted amidyl radicals undergo relatively facile cyclizations.[22-26,33-35] In contrast to the intramolecular H-atom abstraction reaction, there would appear to be a preference for cyclization onto a C=C double bond in the acyl side chain rather than onto a double bond in the alkyl side chain.[25,26] For example,[26] in the chromous



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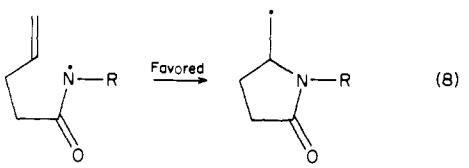


(8)

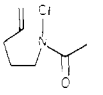
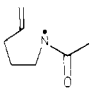
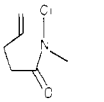
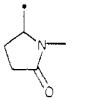
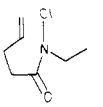
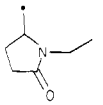
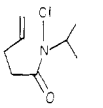
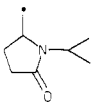
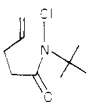
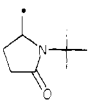
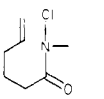
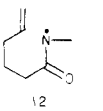
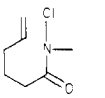
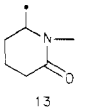
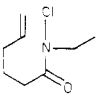
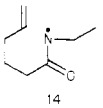
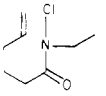
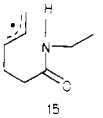
chloride promoted cyclization of olefinic *N*-chloro amides, the compound CH_2=$CH(CH_2)_2CONClCH_3$ gave only cyclized product (five-membered ring) whereas the compound CH_2=$CH(CH_2)_3NClCOCH_3$ gave just 6% of cyclized product (five-membered ring) together with 90% of the uncyclized parent amide.[36] This preference has been explained[26] in terms of steric interactions that, an examination of molecular models quickly reveals, must be much greater for cyclization onto the alkyl moiety than onto the acyl moiety.

These results of Lessard et al.[26] also serve to confirm earlier data[23,24] that had shown that amidyl radicals exhibit the usual free-radical preference for exo rather than endo cyclization,[6,37] i.e., for cyclization to occur at that terminus of the double bond that will make a new radical center external to the new ring. There is also a preference for the formation of five-membered rather than six-membered rings. For example,[24] photolysis of CH_2=$CH(CH_2)_3NClCOCH_3$ in benzene gave 35% of cyclized product whereas no cyclized product was obtained from CH_2=$CH(CH_2)_4NClCOCH_3$. Finally, in intermolecular additions of amidyl radicals to C=C double bonds, there is abundant evidence that steric hindrance of the amidyl disfavors addition.[38]

In view of the facts outlined above, we chose for examination the seven chloro amides listed in Table II. Photolysis of *N*-chloro-*N*-(pentenyl)acetamide in cyclopropane gave the amidyl radical **7** at low temperatures. Photolysis of a fresh sample of chloro amide at 233 K gave only the first two lines of the spectrum of **7** before the chloro amide was consumed. Although no alkyl radical was observed, the same arguments as those used above for the intramolecular H-atom abstraction reactions imply that the rate constant for the cyclization of **7**, k_7 (R' = Me), is ca. 500 s^{-1} at ca. 220 K.

As was expected, the corresponding *N*-methyl-3-butenecarboxamidyl radical was found to cyclize much more readily. Photolysis of its parent chloro amide gave a radical that could only be the cyclized, primary alkyl, radical **8** (see Table II). This radical was formed even at temperatures as low as 143 K, which implies that the rate constant for this ring closure, k_8 (R = Me), must be $\geq 10^3$ s^{-1} at this temperature. Photolysis of *N*-ethyl- and *N*-isopropyl-*N*-chloro-3-butenecarboxamides at ca. 143 K also gave only the cyclized, primary alkyl radicals **9** and **10**, respectively. Thus, k_8 (R = Et) and k_8 (R = *i*-Pr) are also $\geq 10^3$ s^{-1} at 143 K. The corresponding *N*-*tert*-butyl chloro amide also gave only the primary alkyl radical **11**, but the spectral quality was poor at very

Table II. Cyclizations onto C=C Double Bonds: Structure and EPR Parameters of Radicals Observed during Photolysis of Some Appropriate Chloro Amides in Cyclopropane[a]

chloro amide	radical	T, K	g	a^N	a^H
	 7	180	*b*	15.0	32.5 (2)
	 8	223	2.0026	3.5	22.1 (2) 14.6 (1)
	 9	173	2.0026	3.6	22.0 (2) 12.8 (1)
	 10	144	2.0025	4.0	22.0 (2) 9.5 (1)
	 11	233	2.0025	2.75	22.0 (2) 12.0 (1)
	 12	143	*b*	15.0	29.5 (2)
	 13	213	2.0026	4.0	24.0 (1) 22.0 (2) 2.0 (2)
	 14	143	*b*	15.0	40.0 (2)
	 15	193	*b*		14.5 (1) 13.7 (2) 13.5 (2) 4.0 (1)

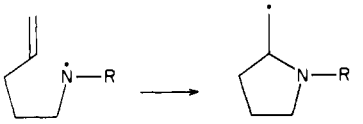
[a] Hyperfine splittings (hfs) are given in gauss; the numbers in parentheses in the a^H column refer to the number of equivalent hydrogen atoms. [b] Not measured.

(33) Forrester, A. R.; Ingram, A. S.; Thomson, R. H. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2847-2853.
(34) Glover, S. A.; Goosen, A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1348-1356.
(35) Glover, S. A.; Goosen, A. *Prog. Theor. Org. Chem.* **1977**, *2*, 297-309.
(36) There is always some question as to whether or not amidyl radicals generated by such techniques are coordinated with the metal center.[28] That is, they may not be really "free" radicals.
(37) Beckwith, A. L. J.; Easton, C. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482-483.
(38) Lessard, J.; Mondon, M.; Touchard, D. *Can. J. Chem.* **1981**, *59*, 431-450.

low temperatures. However, although an *N-tert*-butyl amidyl radical should be readily observable by EPR spectroscopy, one could not be detected at 198 K. From this fact we conclude that k_8 (R = *t*-Bu) is $\geq 5 \times 10^3$ s^{-1} at this temperature.

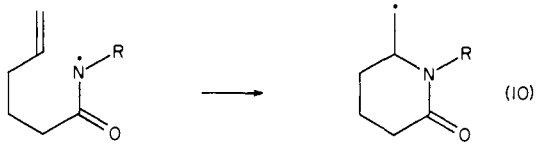
Despite its obvious limitations, the best available model for reactions 7 and 8 for which the Arrhenius parameters are reliably known is the cyclization of the 5-hexenyl radical to form the cyclopentylmethyl radical.[6,39,40] For this reaction the Arrhenius preexponential factor is $10^{10.37}$ s^{-1}.[39] Utilizing this A factor for reaction 7 and the approximate rate constant for this reaction, which is given above yields an activation energy E_7 (R′ = Me) $\approx$ 7.7 kcal/mol and a value for k_7 (R′ = Me) of ca. 5×10^4 s^{-1} at 300 K. For reaction 8, the rigidity of the amidyl moiety is expected to increase the A factor to ca. $10^{11.0}$ s^{-1}, which, in conjunction with the rate constant limits listed above, yields E_8 (R = Me, Et, and *i*-Pr) $\leq$5.2 kcal/mol, E_8 (R = *t*-Bu) $\leq$ 6.6 kcal/mol, and k_8 (R = Me, Et, *i*-Pr) $\geq 1 \times 10^7$ s^{-1}, k_8 (R = *t*-Bu) $\geq 1 \times 10^6$ s^{-1} at 300 K.

The carbonyl group in amidyl radicals produces a very large enhancement of the rates of both reactions 7 and 8 relative to the rate of the analogous cyclization of alkenyl alkyl aminyl radicals, reaction 9. For this reaction, E_9 (R = *n*-Pr) is $\geq$12.5 kcal/mol and k_2 (R = *n*-Pr) is <5 s^{-1} at 300 K.[4]



(9)

Since the 6-heptenyl radical cyclizes at only about 10% of the rate at which the 5-hexenyl radical cyclizes,[6,40] we decided to investigate the photolysis of *N*-chloro-*N*-methyl-4-pentenecarboxamide. At 143 K, the amidyl radical **12** (R = Me) was observed, as we had hoped (see Table II). As the temperature was raised through the 163–193 K range, the intensity of the amidyl radical spectrum decreased, and a new radical made its appearance, becoming the only radical observable at $T >$ 193 K. The new radical has a complex spectrum and a g factor of 2.0026, which indicates that it is carbon centered. We interpret the spectrum as being due to the cyclized primary alkyl radical **13** (R = Me). Our results imply that k_{10} (R = Me) $\approx 10^3$ s^{-1} at

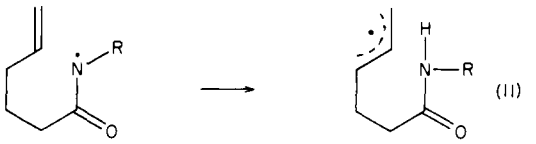


(10)

12 (R=Me) 13 (R=Me)

178 K. The preexponential factor for reaction 10 can be assigned a value of ca. $10^{10.4}$ s^{-1}, which then yields E_{10} (R = Me) $\approx$ 6.0 kcal/mol and k_{10} (R = Me) $\approx 1 \times 10^6$ s^{-1} at 300 K.

We expected that the kinetics of reaction 10 could be more accurately investigated by using *N*-chloro-*N*-ethyl-4-pentenecarboxamide since we have found that *N*-ethyl chloro amides always give better resolved EPR spectra than the *N*-methyl compounds. At 143 K, the expected amidyl radical, **14** (R = Et), was observed (see Table II). At 163 K, a new radical was also present that became the only observable radical at temperatures of 173 K and above. The new radical was carbon centered, its spectrum was fairly intense, and the samples survived prolonged photolysis. The spectral parameters for this radical (see Table II) are clearly not those of the expected cyclized, primary alkyl radical **13** (R = Et). Instead, we attribute the spectrum to an allyl radical to which we assign structure **15** (R = Et). This structure implies that the allyl radical is formed by the intramolecular reaction 11. We rule out the potential alternative of

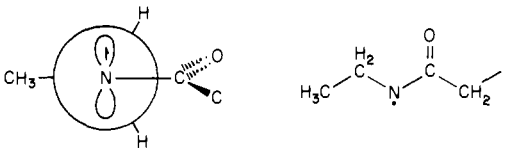


(11)

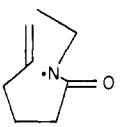
14 (R=Et) 15 (R=Et)

an N-chlorinated allyl radical, which could be formed by an intermolecular H-atom abstraction from the parent chloro amide, on the grounds that a similar species should have been formed from **12** (R = Me) and, more particularly, should have been formed on photolysis of *N*-chloro-*N*-(4-pentenyl)acetamide. This last compound gave, however, only the amidyl radical **7** even at temperatures as high as 233 K (vide supra).

Why does **14** (R = Et) undergo intramolecular H-atom abstraction (reaction 11) whereas **12** (R = Me) undergoes cyclization (reaction 10)? The answer would appear to lie in the unfavorable geometry of the transition state that would be required for **14** (R = Et) to cyclize. The two large β-H hfsc of 40 G for **14** (R = Et) (see Table II) show that this amidyl, like other *N*-ethyl amidyl radicals,[32] adopts a conformation in which the methyl moiety of the *N*-ethyl group lies approximately in the N $2p_z$ nodal plane. Furthermore, steric factors ensure that the methyl group is anti with respect to the carbonyl oxygen, i.e.:



This local conformation implies that in the transition state for addition there will be a large and very unfavorable steric interaction between the methyl group and the CH_2 terminus of the double bond; i.e.:



Cyclization is therefore retarded, and the amidyl radical decays instead by an intramolecular abstraction of a weak allylic hydrogen atom. That this reaction does not occur to an observable (by EPR) extent for **12** (R = Me) illustrates how subtle the factors that govern intramolecular free-radical reactions can be.[6,40,41]

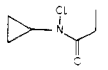
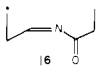
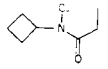
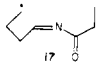
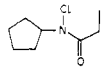
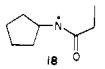
Taking the rate constant for reaction 11 to be ca. 10^3 s^{-1} at 163 K and assuming that $A_{11} \approx 10^{11.0}$ s^{-1}, yield E_{11} (R = Et) $\approx$ 6.0 kcal/mol and k_{11} (R = Et) $\approx 5 \times 10^6$ s^{-1} at 300 K.

Before leaving the subject of amidyl radical addition to C=C double bonds, we note that all our attempts to observe intermolecular examples of these reactions by using EPR spectroscopy were unsuccessful. Thus, for example, only the appropriate amidyl radicals were detected upon photolysis of EtN(Cl)COEt or MeN(Cl)CO-*t*-Bu in the presence of norbornene (a strained olefin), 1,1-diphenylethylene (which would yield a resonance-stabilized adduct radical), and 1,1-dicyclopropylethylene (which would yield a readily detectable, rearranged primary alkyl radical). These results are consistent with product studies that show that *N*-alkyl amidyls are relatively unreactive in intermolecular additions.[28,38]

Ring Opening of *N*-Cycloalkylamidyl Radicals. The photolysis of *N*-nitroso-*N*-cyclopropyl-4-methylphenylcarboxamide in CH_3OH at 253 K has been shown to give products that arise exclusively from the opening of the cyclopropyl ring.[29] It was therefore no surprise to find that the photolysis of *N*-chloro-*N*-cyclopropylpropionamide in cyclopropane at 183 K (the lowest

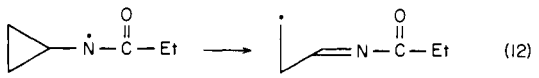
(39) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.
(40) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073–3100.
(41) There was, unfortunately, insufficient material for an analysis of the products of photolysis of the *N*-methyl- and *N*-ethyl-*N*-chloro-4-pentenecarboxamides.

Table III. Ring Openings: Structure and EPR Parameters of Radicals Observed during Photolysis of Some Appropriate Chloro Amides in Cyclopropane[a]

chloro amide	radical	T, K	g	a^N	a^H
	 16	183	*b*		28.2 (2) 22.5 (2)
	 17	143	2.0027		30.0 (2) 21.9 (2)
	 18	243	*b*	15.0	29.0 (1)

[a] Hyperfine splittings (hfs) are given in gauss; the numbers in parentheses in the a^H column refer to the number of equivalent hydrogen atoms. [b] Not measured.

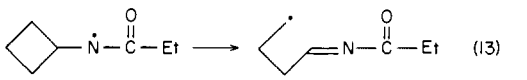
temperature at which this compound would stay in solution) gave a spectrum that we attribute to the primary alkyl radical **16** (see


(12)

16

Table III). Our results with the *N*-cyclobutylpropionamidyl radical (vide infra) lead us to believe that reaction 12 is considerably faster than the ring openings of a number of *N*-alkylcyclopropylaminyl radicals, for which only the ring-opened, primary alkyl radical can be observed by EPR at temperatures as low as 135 K.[4] That is, we believe $k_{12} \gg 10^3$ s^{-1} at 135 K, which, taking A_{12} to be $10^{12.48}$ s^{-1} by analogy with the ring opening of the cyclopropylmethyl radical,[42] yields $E_{12} \ll 5.8$ kcal/mol and $k_2 \gg 2 \times 10^8$ s^{-1} at 300 K.

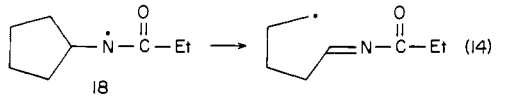
The *N*-*n*-propyl-*N*-cyclobutylaminyl radical undergoes ring opening in the temperature range 198–247 K, which allowed the rate constant for this process to be determined by kinetic EPR spectroscopy. In contrast, photolysis of *N*-chloro-*N*-cyclobutylpropionamide gave only the primary alkyl radical **17** (see Table


(13)

17

III) even at temperatures as low as 130 K (cyclopropane–ethylene solvent). If we assume that A_{13} has the same value (viz., $10^{12.8}$ s^{-1}) as that found for ring opening of the *N*-*n*-propyl-*N*-cyclobutylaminyl radical,[4] then $E_{13} < 5.8$ kcal/mol and $k_{13} > 4 \times 10^8$ s^{-1} at 300 K.

The high rate for reaction 13 led us to explore the possibility that the corresponding cyclopentylpropionamidyl radical **18**, would

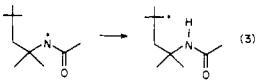
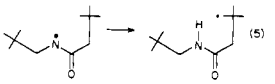
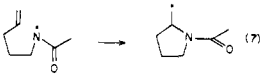
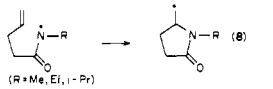
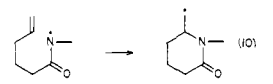
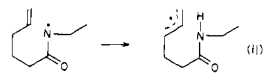
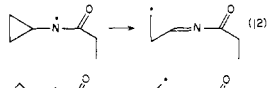
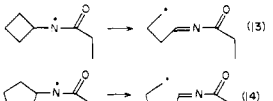
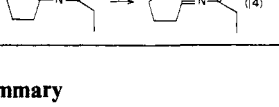

(14)

18

also undergo ring opening. Such, however, was not the case at temperatures up to 243 K, the highest temperature at which radicals would be observed on photolysis of the parent chloro amide, only **18** being detectable (see Table III). If we assume that A_{14} has a value of 10^{13} s^{-1}, then $E_{14} > 11$ kcal/mol and $k_{14} < 8 \times 10^4$ s^{-1} at 300 K.

(42) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024–7026.

Table IV. Summary of Approximate Kinetic Data for the Amidyl Radical Horlogerie

reaction	log A, s^{-1} (assumed)	E, kcal/mol	k, s^{-1} at 300 K
 (3)	10.6	7.7	1×10^5
 (5)	11.2	9.1	4×10^4
 (7)	10.4	7.7	5×10^4
 (8) (R = Me, Et, i-Pr)	11.0	≤ 5.2	$\geq 1 \times 10^7$
 (10)	10.4	6.0	1×10^6
 (11)	11.0	6.0	5×10^6
 (12)	12.5	$<<5.8$	$>>2 \times 10^8$
 (13)	12.8	<5.8	$>4 \times 10^8$
 (14)	13.0	>11	$<8 \times 10^4$

Summary

Our search for an amidyl radical clock that could be precisely calibrated by kinetic EPR spectroscopy did not succeed. However, we did manage to obtain approximate or limiting rate constants at specific temperatures for a variety of unimolecular amidyl radical reactions. Combination of this kinetic data with estimated Arrhenius preexponential factors for the reactions in question provides some preliminary stock for an amidyl radical horlogerie. The data for this horlogerie are summarized in Table IV. They provide quantitative evidence supporting the qualitative observation that amidyl radicals are much more reactive in unimolecular processes than are dialkylaminyl radicals.

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Registry No. 1, 82871-05-4; **2**, 82871-06-5; **4**, 82871-07-6; **5**, 82880-35-1; **6**, 82871-08-7; **7**, 82871-09-8; **8**, 82871-10-1; **9**, 82871-11-2; **10**, 82871-12-3; **11**, 82871-13-4; **12**, 82871-14-5; **13**, 82871-15-6; **14**, 82871-16-7; **15**, 82871-17-8; **16**, 82871-18-9; **17**, 82871-19-0; **18**, 82871-20-3; H_2, 1333-74-0; $H_2C{=}CH(CH_2)_2CONMe$, 82871-21-4; $H_2C{=}CH(CH_2)_2CONEt$, 82871-22-5; $H_2C{=}CH(CH_2)_2CONPr$-*i*, 82871-23-6; $H_3C(CH_2)_3C(Me_2)N(Cl)Ac$, 55281-84-0; *t*-$BuCH_2C(Me_2)N(Cl)Ac$, 62024-41-3; *t*-$BuCH_2C(Me_2)N(Cl)COBu$-*t*, 82871-26-9; *t*-$BuCH_2N(Cl)COCH_2Bu$-*t*, 82871-27-0; $H_2C{=}CH(CH_2)_3N(Cl)Ac$, 54385-04-5; $H_2C{=}CH(CH_2)_2CON(Cl)Me$, 66769-76-4; $H_2C{=}CH(CH_2)_2CON(Cl)Et$, 82871-28-1; $H_2C{=}CH(CH_2)_2CON(Cl)Pr$-*i*, 82871-29-2; $H_2C{=}CH(CH_2)_2CON(Cl)Bu$-*t*, 82871-30-5; $H_2C{=}CH(CH_2)_3CON(Cl)Me$, 82871-31-6; $H_2C{=}CH(CH_2)_3CON(Cl)Et$, 82871-32-7; (ethylcarbonyl)cyclopropylamidogen, 82871-24-7; (ethylcarbonyl)cyclobutylamidogen, 82871-25-8; *N*-chloro-*N*-cyclopropyl-2-oxopropanamine, 82871-33-8; *N*-chloro-*N*-cyclobutyl-2-oxopropanamine, 82871-34-9; *N*-chloro-*N*-cyclopentyl-2-oxopropanamine, 82871-35-0.