

ELECTRON SPIN RESONANCE STUDIES OF  
TRANSIENT AMIDO AND SULFONAMIDO FREE RADICALS

by

ROLAND WERNER GELLERT

Diplom-Chemiker-Vorpruefung, 1970  
Justus-Liebig Universitaet, Giessen

333  
1226-5600

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A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1973

Approved by:

Wayne C. Blauen  
Major Professor

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Doc.

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## I. PART I: TRANSIENT AMIDO FREE RADICALS

### A. Introduction

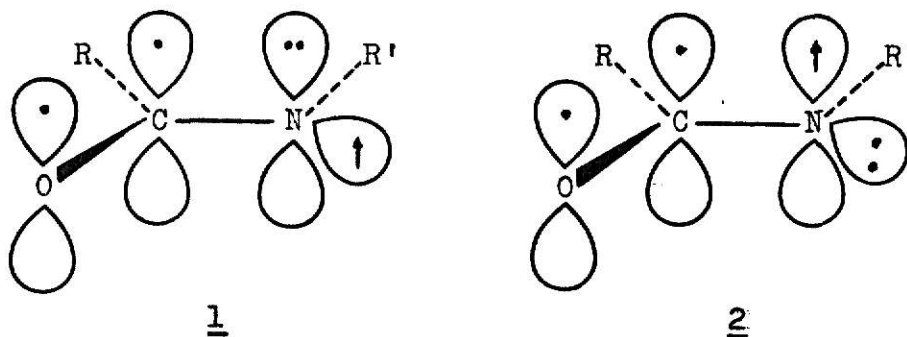
Amido or acylamino radicals of the general structure  $RC(O)-\dot{N}-R'$  ( $R, R' = H, \text{ alkyl}$ ) have received considerable attention in synthetic organic chemistry during the last few years as possible intermediates in photoinduced rearrangement reactions. It was found that N-alkyl-N-haloamides of the type:  $R-N(\text{Hal})-CO-R'$  ( $\text{Hal} = \text{Cl or Br}$ ) rearranged to the corresponding haloalkyl isomers upon irradiation in a manner analogous to the free radical Hofmann-Loeffler reaction of protonated N-chloroamines.<sup>1,2</sup> These photolytic conversions opened a convenient route for the syntheses of  $\gamma$ -lactones and iminolactones upon treatment of the haloalkylamides with base or acid, respectively.<sup>3,4,5</sup> Likewise, it was found that N-chloroamides added to olefins upon irradiation to afford N-alkyl- $\beta$ -chloroalkylamides<sup>1</sup> and similarly, that N-methyl-N-nitrosoamides,  $\text{CH}_3-N(\text{NO})-CO-R$ , underwent an intramolecular addition reaction if a double bond in the alkyl side chain R was present to produce the corresponding N-methyl-lactam upon irradiation.<sup>6</sup> Additionally, bromination of the benzene ring was found to occur in the photoinitiated rearrangement reactions of N-bromoacetanilide and N-bromo-2,4,6-trichloroacetanilide.<sup>7</sup>

These reactions were most conveniently explained by assuming a photolytically produced amido radical intermediate that underwent rapid rearrangement and abstraction reactions, accounting for the observed products. Although these studies seemed to confirm the existence of amido radicals, their electronic structure had been

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the subject of considerable controversy. The two figures below illustrate the possible electron distribution in question:



In terms of the definition given by Norman and Gilbert,<sup>8</sup> structure 1 could be classified as a  $\Sigma$  radical<sup>9</sup> in which the spin bearing orbital on nitrogen would be orthogonal to the adjacent  $\pi$ -system of the carbonyl group (similar to the  $\Sigma$  phenyl radical). On the other hand, in the  $\Pi$  radical as illustrated by 2 the unpaired electron would reside in a 2p orbital on nitrogen in conjugation with the  $\pi$ -system of the carbonyl group.

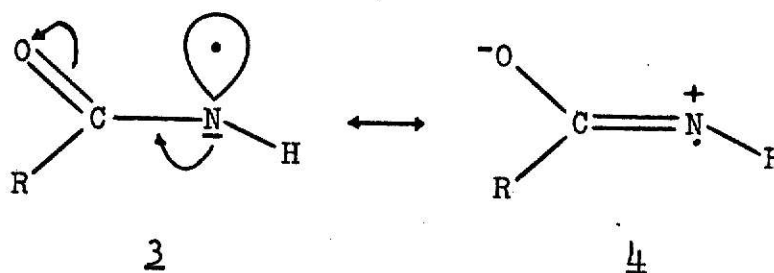
The basic question had been whether the difference in energy resulting from the delocalization of a pair of electrons in a p orbital would be sufficiently great to overcome the promotional energy of an electron in a hybrid orbital to a p orbital or, in other words whether conjugational effects with a  $\pi$ -system were energetically more favorable than possession of finite s-character in a hybrid orbital for an unpaired electron.

The chemical implications of these different electronic configurations were of some significance for the prediction of reaction modes of the radicals. It had been pointed out by Hedaya and his co-

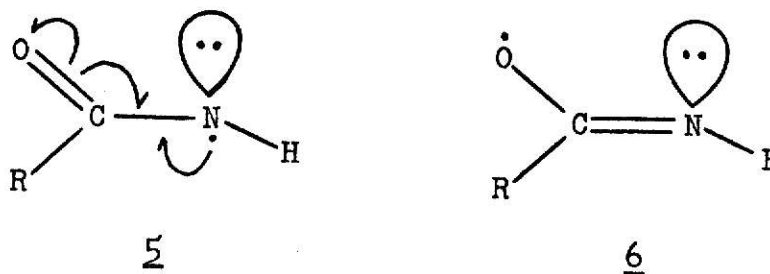
workers<sup>10</sup> that a conjugated  $\Pi$  radical would exhibit ambient reactivity whereas the  $\Sigma$  radical which was characterized by predominant localization of spin at one site should react at this site. In general, a  $\Sigma$  radical should be more reactive and less selective than a  $\Pi$  radical.

Purported evidence for both a  $\Sigma$  and a  $\Pi$  electronic configuration was reported on the basis of theoretical, kinetic, and electron spin resonance (esr) studies but the literature was confusing and frequently misassignments of esr spectra occurred.

On the basis of simple molecular orbital theory Hedaya, *et al.*,<sup>10</sup> predicted that amido radicals should be  $\Sigma$  radicals, a result they found consistent with qualitative considerations of valence bond structures for the  $\Sigma$  state:



Electron pair delocalization should be highly important because of the more favorable distribution of charge in the excited Lewis structure 4 in contrast to the delocalization of merely one electron in a  $\Pi$  electronic state that would not account for the higher electro-



negativity of oxygen compared with nitrogen (structures 5 and 6). Product studies of the photoinduced decomposition of N,O-diacylhydroxylamines,  $R-C(O)-NH-OC(O)-R'$ , were interpreted in terms of a  $\Sigma$  electronic ground state of acylamino radicals by Danieli, *et al.*<sup>11</sup>

Electron spin resonance evidence for the existence of amido radicals was first reported in 1966 by Lontz.<sup>12</sup> Upon  $\gamma$ -irradiation of pentafluoropropionamide strong absorption signals were obtained that were assigned to a carbon-centered radical,  $CF_3-\dot{C}F-C(O)-NH_2$ , but the spectrum also showed features of a second radical. These weak secondary lines were interpreted to be due to the amido radical  $CF_3-CF_2-C(O)-\dot{N}H$ , with an approximate hyperfine splitting constant (hfsc) for nitrogen of ca. 30 gauss, indicating significant spin density on nitrogen. This was not investigated further.

In the same year Smith and Wood<sup>13</sup> assigned an esr spectrum obtained by hydroxyl radical attack on formamide to the acylamino radical  $HC(O)-\dot{N}H$ . Later, however, it was shown by Livingston and Zel-des<sup>14</sup> that the  $\Sigma$  acyl radical  $H_2N-\dot{C}(O)$  was formed instead of the acylamino radical. This interpretation was supported by Yonezawa and his coworkers<sup>15</sup> who observed similar carbamoyl radicals of the general structure  $\dot{C}(O)-NR_2$  ( $R = H, CH_3$ ) upon hydrogen abstraction from different substituted formamides.

A radical produced upon x-irradiation of hydroxyurea was initially reported to be the  $H_2N-C(O)-\dot{N}H$  radical by Shields, Hamrick, and Redwine,<sup>16</sup> but the assignment was later rejected by Fox and Smith<sup>17</sup> and the spectrum suggested to be due to the corresponding nitroxide,  $H_2N-C(O)-NH\dot{O}$ . Symons and his coworkers<sup>18</sup> gave more reli-

able evidence for a nitrogen-centered radical derived from urea and suggested it to be a  $\Pi$  radical,  $\text{H}_2\text{N}-\text{C}(\text{O})-\dot{\text{N}}\text{H}$ . But the electron-donating  $\text{NH}_2$ -group must interact strongly with the carbonyl group to effectively dampen its electron-withdrawing capability and this species could not be considered truly representative of simple amido radicals.

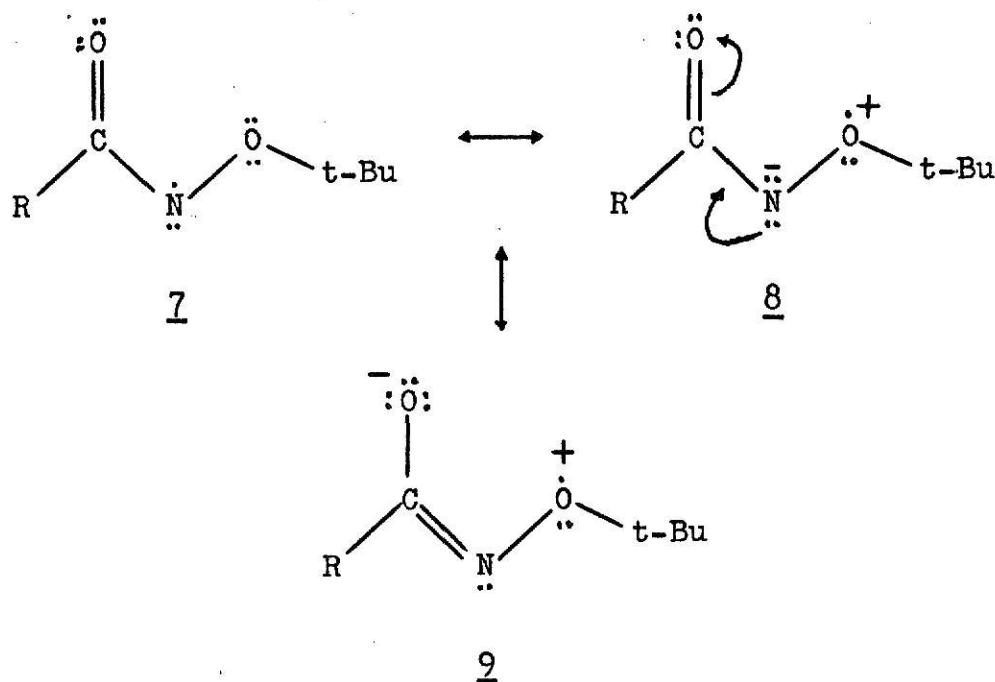
Several reports appeared in the literature of radicals derived from x- and  $\gamma$ -irradiated single crystals of malonamide,  $(\text{H}_2\text{N}-\text{C}(\text{O})-)_2\text{CH}_2$  and dicyandiamide,  $\text{N}\equiv\text{C}-\text{N}=\text{C}(\text{NH}_2)_2$ . The original assignment of a radical from malonamide to the structure  $\text{H}_2\text{N}-\text{C}(\text{O})-\text{CH}_2-\text{C}(\text{O})-\dot{\text{N}}\text{H}$  by Cyr and Lin<sup>19,20</sup> found support in the work of Straw and Moulton.<sup>21</sup> These workers suggested a  $\Sigma$  electronic configuration at the radical center, a conclusion that was questioned by Symons<sup>22</sup> who favored the idea, based on theoretical expectations, that radicals of the type  $\text{RC}(\text{O})-\dot{\text{N}}\text{H}$  were much more likely  $\Pi$  than  $\Sigma$ . This point of view was supported by Lau and Lin<sup>23</sup> who postulated the radical derived from dicyandiamide to be of the structure  $\text{N}\equiv\text{C}-\text{N}=\text{C}(\text{NH}_2)\dot{\text{N}}\text{H}$  and claimed that the spin bearing orbital was a  $\Pi$  molecular orbital.

These conflicting reports arose from an unusual large and approximately isotropic hfsc due to one hydrogen (ca. 73 - 81 G). Lind and Kewley<sup>24</sup> attempted to explain the formation of possibly two types of radicals ( $\Pi$  and  $\Sigma$ ) from the same  $\text{NH}_2$ -group by geometrical considerations stemming from hydrogen bonding in the crystal which could force one hydrogen atom out of the plane of the molecule thus affecting the hybridization at the nitrogen radical center.

More recent results, however, indicated that misassignments of

spectra occurred. Lin and his coworkers,<sup>25</sup> based on  $^{15}\text{N}$ -labelling studies, commented that radiation damage in crystals of compounds containing amido and/or nitrile groups led to the formation of imino radicals,  $\dot{\text{N}}=\text{CHR}$ , an interpretation that was supported by Symons<sup>26</sup> who pointed out the importance of imino radicals as intermediates in photolytic reactions.

Solution esr studies of radicals comparable to simple amido radicals were done by Koenig, *et al.*<sup>27</sup> These workers observed N-*tert*-butoxyamido radicals,  $\text{R}-\text{C}(\text{O})-\dot{\text{N}}-\text{t-Bu}$  ( $\text{R} = \text{alkyl, aryl}$ ), and classified them as II radicals. But the alkoxy substituent attached directly to nitrogen could conceivably bias these species in favor of a II structure.



From resonance structures shown above it seemed more likely that electron pair delocalization into the carbonyl group from nitrogen

should be predominant for these species as shown in 8 and 9, illustrating the influence of the hetero atom oxygen with its lone pairs of electrons on the electron distribution.

Esr evidence for simple amido radicals in solution was published by Tordo and his coworkers<sup>28,29</sup> in the early stages of this project. Irradiation of diacyltetrazenes,  $(R-C(O)-N(R')-N=)_2$ , and N-nitrosoamides,  $R-C(O)-N(NO)-R'$ , at low temperatures in toluene yielded spectra that were assigned to the corresponding N-alkylamido radicals,  $R-C(O)-\dot{N}-R'$ . The small hfsc's ( $a^N = 7$  G and  $a_{NCH_3}^H = 8$  G) were interpreted in terms of a II electronic ground state of acylamino radicals but as the reported g values of 2.0065 - 2.0066 were similar to the values obtained for acyl nitroxides,<sup>30</sup>  $R-C(O)-N(\dot{O})-R'$ , the results were viewed with circumspection in this laboratory.

## B. Discussion of Results

### 1. General Aspects

Electron spin resonance (esr) spectroscopy seemed ideally suited to answer the question concerning the electronic structure of amido radicals as it should not only describe the location of the unpaired electron in the molecule but also yield detailed information concerning the type(s) of orbital in which the electron might reside.

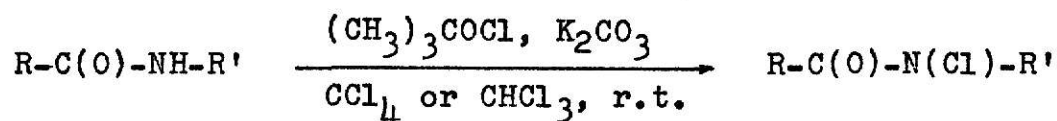
In a II electronic configuration the unpaired electron was most likely to be found in a 2p orbital on nitrogen with a nodal plane at

the nucleus. The hyperfine interaction should be small and a nitrogen hfsc close to that of dialkylamino radicals,  $R-\dot{N}-R$ , ( $a^N$  ca. 14 gauss)<sup>31</sup> should be observed if significant delocalization of spin onto the carbonyl group did not occur. For a  $\Sigma$  amido radical, however, a much larger hfsc with the nitrogen atom bearing the unpaired electron would be expected due to the non-zero probability of the electron being found at the nucleus.

## 2. Generation and Identification of Amido Radicals

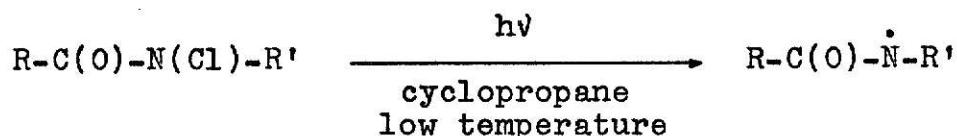
Several experimental routes seemed suitable to generate amido radicals in solution. Potential sources included thermal decomposition or irradiation of N-nitrosoamides,<sup>6,27,29,32,33</sup> photoinduced abstraction reactions by tert-butoxy radicals from amides,<sup>27</sup> photolytical cleavage of diacyltetrazenes,<sup>28,34</sup> or tert-butyl-N-acylpercarboxylates,<sup>10</sup> and uv-irradiation of N-haloamides.<sup>1,2,4,5,27</sup> The later method, using N-chloro derivatives, was chosen since the relatively weak N-Cl bond the binding energy of which had been estimated to be ca. 45 kcal/mol<sup>35</sup> was expected to undergo facile homolytic cleavage upon uv-irradiation to afford the nitrogen-centered radical in a sufficient steady state concentration to allow detection by esr. A comparable method had proven useful in this laboratory when dialkylaminium radical cations were generated upon uv-irradiation of the corresponding N-chloro-dialkylamines in the presence of sulfuric acid.<sup>36</sup> Convenient synthetic routes for the preparation of N-chloroamides existed. Generally the parent amide was treated with tert-butylhypochlorite in the presence of small amounts of potassium car-

bonate in an inert solvent at room temperature for several hours to yield the N-chloro compound:<sup>2,5</sup>



Catalytic amounts of bromine were recommended to shorten the reaction time.<sup>37</sup> Completion of the chlorination could easily be checked by the disappearance of the N-H stretching band in the ir spectrum, disappearance of the amide proton absorption and a characteristic downfield shift of the  $\beta$ -proton in the nmr spectrum (see experimental part for details).

The synthesis of N-chloro-N-tert-butylacetamide and N-chloro-N-methylpivalamide was carried out and esr spectra of nitrogen-centered radicals were obtained by photolyzing 10 - 20% by volume solutions of these N-chloroamides in degassed cyclopropane with a high pressure mercury lamp at low temperatures:



The spectrum in Figure 1 (A) was obtained upon irradiation of N-chloro-N-tert-butylacetamide and showed a 1:1:1 triplet due to the nitrogen nucleus each line split into a 1:3:3:1 quartet, assigned to the aceto methyl group. Partially resolved splittings resulted from interaction with the hydrogens of the tert-butyl substituent. Figure

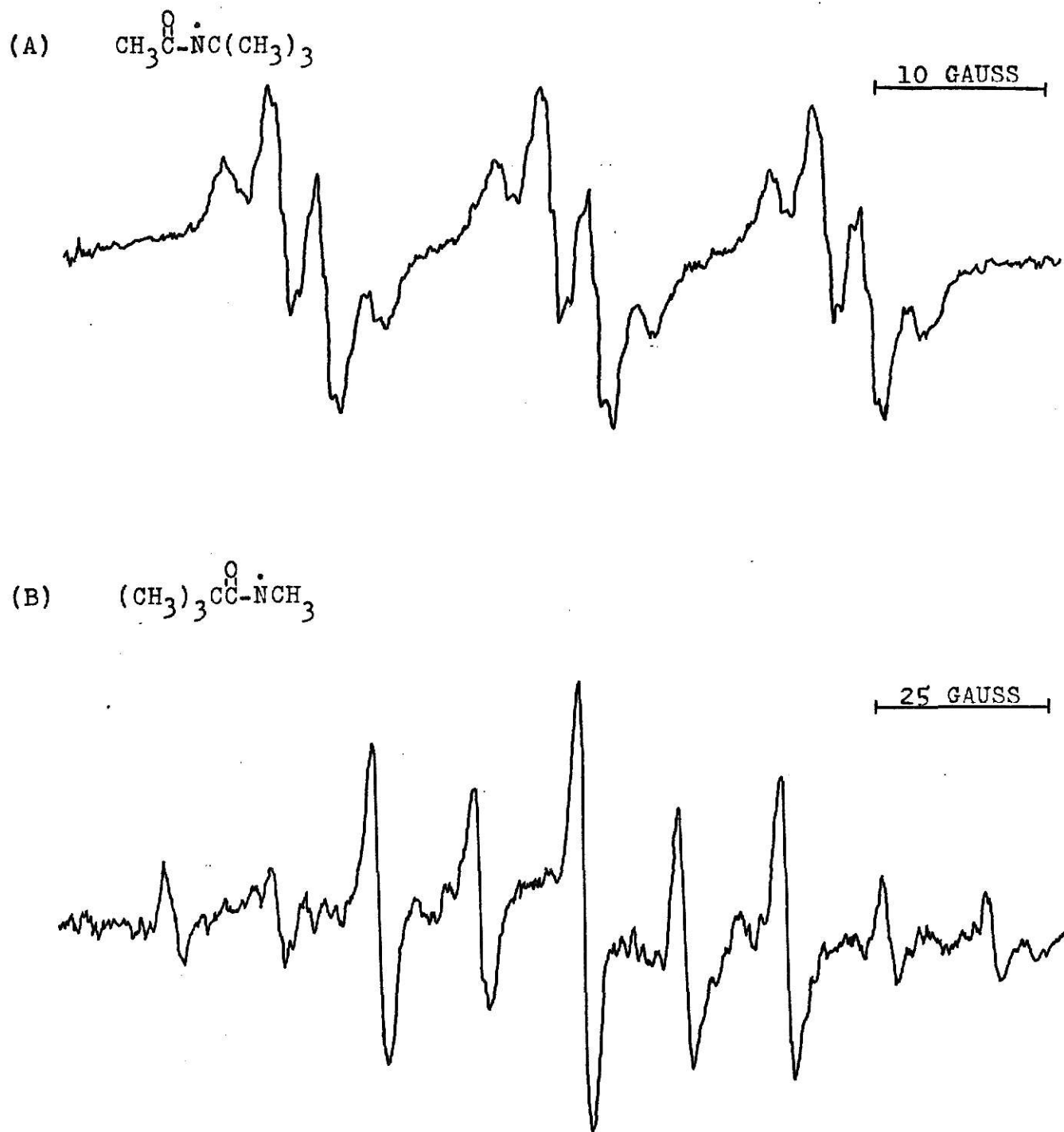


Figure 1. Electron spin resonance spectrum of (A) the N-tert-butyl-amido radical and (B) the N-methylpivalamido radical.

1 (B) showed the spectrum that was assigned to the N-methylpival-amido radical with an intensity distribution of 1:1:4:3:6:3:4:1:1 which was explained in terms of a large 1:3:3:1 quartet due to the N-methyl hydrogen atoms, each line split into a 1:1:1 triplet by one nitrogen nucleus, the hfsc for the hydrogen atoms being approximately twice as large as the nitrogen hfsc. A satisfactory computer simulated spectrum<sup>38</sup> including second order effects<sup>39</sup> was obtained on the basis of this interpretation. ESR spectral parameters are summarized in Table I.

Table I

Spectral Parameters<sup>a</sup> of Simple Amido Radicals

Radical	$a^N$	$a^H^b$	$g \text{ value}^c$	Temp., °C
$\text{CH}_3\text{C}(\text{O})\dot{\text{N}}\text{C}(\text{CH}_3)_3$	15.70	2.71	2.0044	-40
$(\text{CH}_3)_3\text{CC}(\text{O})\dot{\text{N}}\text{CH}_3$	15.00	29.30	2.0053	-100

<sup>a</sup> Hfsc's reported in gauss, estimated accuracies  $\pm 0.7\%$

<sup>b</sup> Interaction with three hydrogens

<sup>c</sup> Corrected to second order effects, estimated accuracy  $\pm 0.0001$

The derived data were interpreted in terms of a II electronic ground state of amido radicals.<sup>40</sup> The magnitudes of the splitting constants due to nitrogen and the N-methyl hydrogens, ca. 15 G and 29.30 G respectively, seemed consistent with other nitrogen-centered II radicals. Koenig and his coworkers<sup>27</sup> reported nitrogen hfsc's ranging

from 9.60 G to 11.95 G for N-tert-butoxyamido radicals. Likewise, N-alkoxy-N-carboethoxyamino radicals,  $\text{RON}\cdot\text{C}(\text{O})\text{-OC}_2\text{H}_5$ , which were viewed as substituted acylamino radicals where the substituents stabilize the II nature of the radicals, had nitrogen hfsc's of 10.80 G.<sup>41</sup> Additionally, results from investigations of other nitrogen-centered II radicals in this laboratory in which the radical center was not adjacent to a carbonyl group confirmed this interpretation. Nitrogen hfsc's for simple dialkylamino radicals and the corresponding dialkylaminium radical cations,  $\text{R-NH}^+\text{-R}$ , were reported to be of the order of magnitude of 14 G and 18 - 19 G, respectively.<sup>31,36</sup> A similar value was also obtained for the nitrogen hyper-

Table II

Spectral Parameters<sup>a</sup> of Some Nitrogen-Centered II Radicals

Radical	$a^{\text{N}}$	$a^{\text{H}^{\text{b}}}$	g value	Reference
$(\text{CH}_3)_3\text{CC}(\text{O})\dot{\text{N}}\text{CH}_3$	15.00	29.30	2.0053	this work
$\text{CH}_3\text{C}(\text{O})\dot{\text{N}}\text{C}(\text{CH}_3)_3$	15.70		2.0044	this work
$\text{C}_3\text{H}_7\text{C}(\text{O})\dot{\text{N}}\text{OC}(\text{CH}_3)_3$	10.35		2.0058	27
$\text{C}_2\text{H}_5\text{OC}(\text{O})\dot{\text{N}}\text{OC}_2\text{H}_5$	10.80		2.0056	41
$\text{CH}_3\dot{\text{N}}\text{CH}_3$	14.78	27.36	2.0044	31
$\text{CH}_3\dot{\text{N}}^+(\text{H})\text{CH}_3$	19.28	34.27	2.0036	36
$\text{CH}_3\dot{\text{N}}\text{OC}(\text{CH}_3)_3$	14.47	21.51	2.0048	42

<sup>a</sup> Hfsc's reported in gauss

<sup>b</sup> Interaction with three hydrogen atoms

fine interaction in N-alkoxy-N-alkylamino radicals,  $RO-\dot{N}-R'$ .<sup>42</sup> The  $\beta$ -hydrogen spectral parameters for N-methyl substituted radicals were comparable, too, as can be observed from the data in Table II. A smaller  $\beta$ -hydrogen hfsc was expected in the case of the N-tert-butoxy-N-methylamino radical (last entry in Table II) as alkoxy substituent groups should be quite effective in removing spin density from the nitrogen atom.

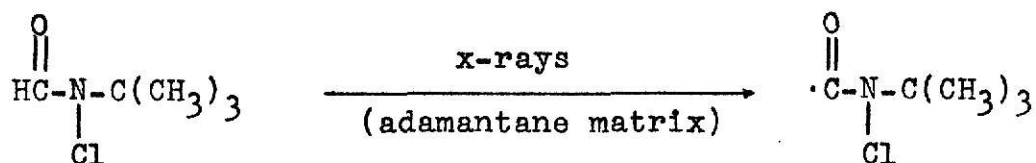
The magnitudes of the hfsc's for the amido radicals reported furthermore suggested that there should not be extensive delocalization of the unpaired electron onto the carbonyl group. For example, carbon-centered  $\alpha$ -keto radicals,  $R-C(O)-\dot{C}(CH_3)-R'$ , had  $\beta$ -hydrogen hfsc's of ca. 22 G (compared to 29.30 G for amido radicals) and the spin density on the carbon radical center was estimated to be approximately 0.77.<sup>43</sup>

The g values of 2.0044 and 2.0053 for the two amido radicals reported gave further evidence for a II electronic structure, although the reason(s) for the difference in g values between the two radical species was not immediately apparent. Their order of magnitude, however, agreed quite well with the other entries in Table II.

As had been noted above, a  $\Sigma$  amido radical would be expected to exhibit a much greater nitrogen hyperfine interaction. For example, iminoxyl radicals,  $R_2C=\dot{N}O$ , have been investigated and nitrogen hfsc's of ca. 30 G were reported,<sup>8,44,45</sup> although only 50% of the spin density seemed to be associated with the nitrogen nucleus. Therefore these species were classified as  $\Sigma$  radicals in which the unpaired electron was contained in an orbital derived from a p orbi-

tal on oxygen and the non-bonding  $sp^2$  orbital on nitrogen lying in the nodal plane of the molecular C-N  $\pi$  bond.

The investigation of N-chloroformamides,  $HC(O)-N(Cl)-R$ , should have revealed additional information about the electronic structure of amido radicals as the hfsc of the formyl proton was expected to be small for a  $\Pi$  radical because this hydrogen would be held in the nodal plane of the 2p orbital on nitrogen and large in case of a  $\Sigma$  configuration due to the alignment of the C-H bond with the spin bearing orbital in the plane of the molecule. However, upon irradiation of N-chloro-N-tert-butylformamide at low temperatures in solution no spectrum could be recorded. In another attempt to generate a formamido radical, the technique of Wood and Lloyd was employed.<sup>46-48</sup> Purified adamantane was dissolved in cyclohexane and freshly distilled N-chloro-N-tert-butylformamide was added. After evaporation of the solvent some of the amide remained trapped in the adamantane matrix. After x-irradiation (copper target, 45 kV, 20 mA) at  $-196^\circ$  for two hours a three line spectrum with an intensity distribution of 1:1:1 was recorded between  $-120^\circ$  and  $+40^\circ$  with a slight intensity increase at above  $0^\circ$ . The parameters derived from the spectrum obtained at  $0^\circ$  (Figure 2) were:  $a^N = 21.57$  G and  $g = 2.0019$ . The relatively small g value and nitrogen hfsc suggested that a carbon-centered  $\Sigma$  radical, most likely the corresponding formyl radical, was produced:



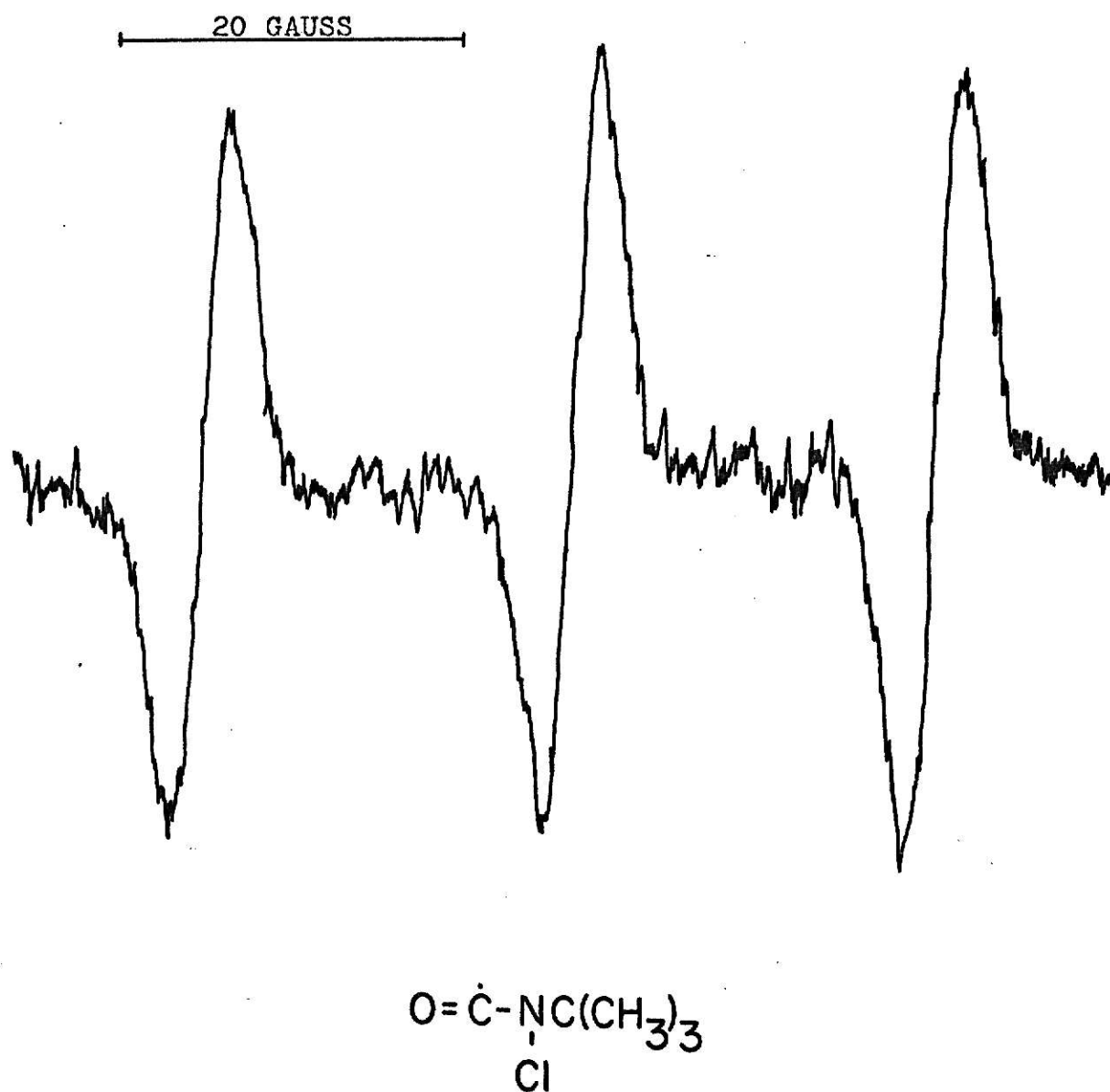


Figure 2. Electron spin resonance spectrum derived from N-chloro-N-tert-butylformamide in an adamantane matrix upon x-irradiation.

Furthermore, the esr spectral data were consistent with other formyl radicals reported in the literature.<sup>14,15</sup> For example, for the unsubstituted formyl radical,  $\dot{C}(O)NH_2$ , a nitrogen hfsc of 21.8 G and a g value of 2.00167 was derived.<sup>15</sup> On the basis of this result it did not seem possible to observe formamido radicals derived from N-chloroformamides as the carbonyl-carbon hydrogen bond was even more labile towards homolytic cleavage than the N-Cl bond.

### 3. Generation and Identification of Acyl Nitroxides

As noted above it was suspected that the spectra obtained by Tordo and his coworkers<sup>28,29</sup> were misinterpreted. In order to reject their assignments two N-chloroamides were photolyzed in air-saturated toluene (ca. 10% by volume) at  $-90^\circ$  using a 25% transmittance screen in front of the uv lamp. Irradiation for ca. 10 sec of these solutions produced strong signals the intensities of which decayed slowly but upon repeated irradiation for a few seconds the initial intensity was regained. The spectrum obtained upon photolysis of N-chloro-N-methylacetamide (Figure 3) exhibited a 1:3:3:1 quartet, each line split into a smaller 1:1:1 triplet. The spectra produced in this manner were assigned to the corresponding acyl nitroxides,  $R-C(O)-N(\dot{O})-R'$ . The identity of these radicals was evidenced by the mode of generation, the relatively small coupling constants for nitrogen and the N-methyl protons, and g values characteristic of nitroxides. Comparison with reported acyl nitroxides confirmed these assignments (Table III).<sup>30,49,50</sup> These results indicated quite clearly that the paramagnetic species reported by Tor-

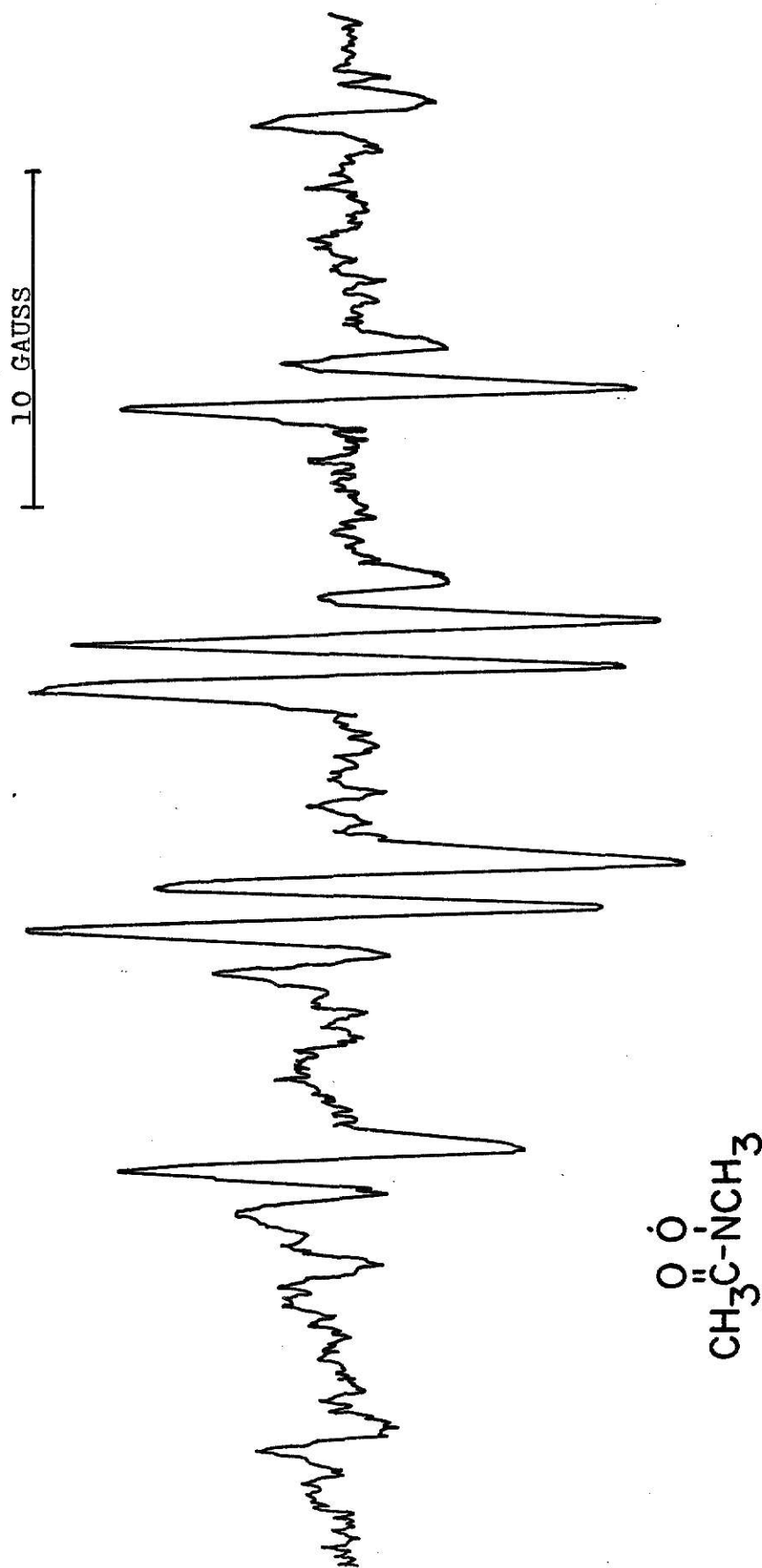


Figure 3. Electron spin resonance spectrum of the N-methylacetyl nitroxide radical.

Table III

Spectral Parameters<sup>a</sup> of Some Acyl Nitroxides

Radical	$a^N$	$a^{NCH_3^H}$	$g$ value	Reference
$CH_3C(O)N(\dot{O})C(CH_3)_3$	7.57		2.0066	this work
$CH_3C(O)N(\dot{O})CH_3$	7.20	8.53	2.0065	this work
$CH_3C(O)N(\dot{O})C(CH_3)_3$	8.0		2.0068	30
$CH_3C(O)N(\dot{O})CH_3^b$	6.9	8.1	2.00655	28,29
$CH_3C(O)N(\dot{O})C(CH_3)_3^b$	7.1		2.00655	29

<sup>a</sup> Hfsc's reported in gauss<sup>b</sup> Reported as the corresponding amido radicals

do, et al.,<sup>28,29</sup> and interpreted as amido radicals (last two entries in Table III) were instead the corresponding acyl nitroxides. The

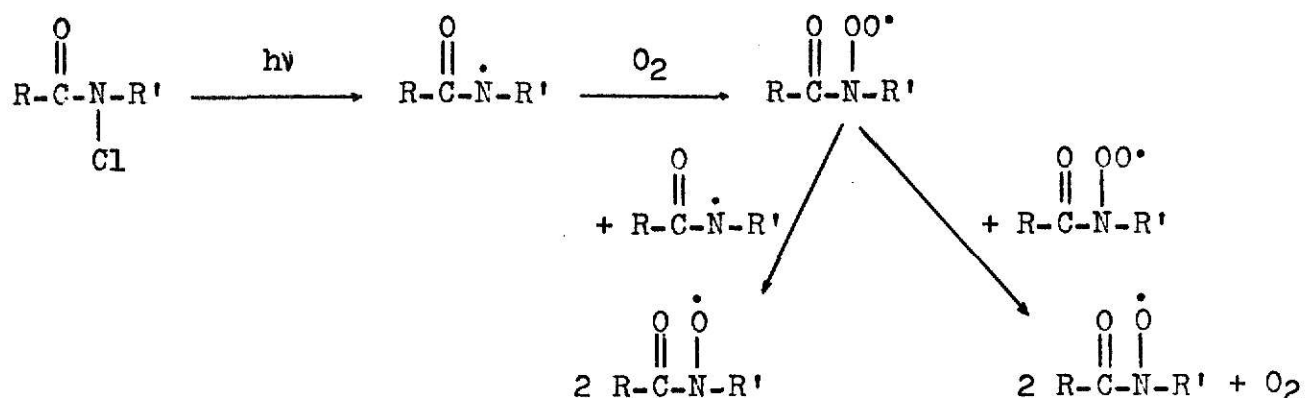


Figure 4. Formation of acyl nitroxides from amido radicals in the presence of oxygen.

formation of nitroxides from N-chloroamides in the presence of air

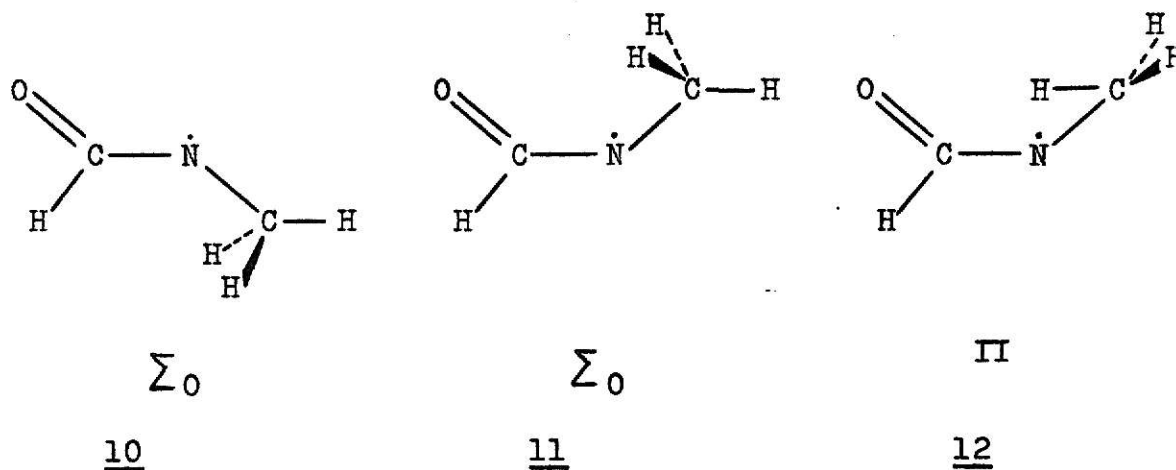
was best explained by assuming the initial formation of an amido radical, attack of oxygen at the radical center that would lead to the formation of a peroxy radical and further reaction with a second amido or peroxy radical to yield the acyl nitroxide.

This observation opened a convenient route for trapping transient amido radicals which could be illustrated by the following example. It was not possible to observe the amido radical derived from N-chloro-N-methylacetamide probably due to the poor solubility of the parent compound at low temperatures or the relative instability of the radical, but the corresponding acetyl nitroxide,  $\text{CH}_3\text{-C}(\text{O})\text{-N}(\dot{\text{O}})\text{CH}_3$ , could be observed in oxygen-rich toluene, indicating that an initial formation of the amido radical occurred. Thus oxygen seemed to be a much simpler spin trapping reagent for acyl radicals (at least in these cases) than the previously reported trap, nitrosobenzene.<sup>51</sup>

#### 4. INDO Calculations

Intermediate neglect of differential overlap (INDO)<sup>52,53</sup> calculations have proved useful in predicting hyperfine coupling constants of nitrogen-centered II radicals.<sup>31,36,41</sup> As spin densities and geometries could be derived from these calculations it was of interest to apply this semiempirical method to amido radicals. However, when performing calculations on the N-methylformamido radical inconsistent results were obtained. Using bond distances and angles from results of electron diffraction studies<sup>54</sup> and Pople's standard "A" geometry<sup>53</sup> for unreported parameters, different electronic configurations for this radical were calculated for very similar conformations as indi-

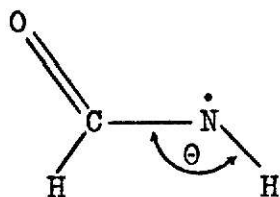
cated by the structures below.<sup>55</sup>



For structures 10 and 11 INDO calculated most spin density on the oxygen atom in the plane of the molecule which was labelled a  $\Sigma_0$  configuration. A very small nitrogen hfsc (ca. 1 - 2 G) but a large formyl hydrogen coupling constant (ca. 70 G) was predicted. Rotation of the methyl group from geometry 11 to 12 completely changed the electron distribution and the total spin density was calculated to be about equally distributed between 2p orbitals on oxygen and nitrogen perpendicular to the plane of the molecule which was indicative of a  $\Pi$  radical in terms of the previous definition. The nitrogen hfsc was calculated to be of the order of 10 G in fair agreement with experimental data. Tordo and his coworkers<sup>28</sup> also derived a  $\Pi$  description from INDO calculations but apparently failed to investigate any alternative conformations. The results from the present INDO calculations were viewed with circumspection as it seemed unlikely that mere rotation of the N-methyl group could have such a significant influence on the spin density distribution. Koenig<sup>56</sup>

traced this discrepancy to the initial density matrix of the INDO method which was derived from a form of Extended Huckel Theory. The latter method predicted the lowest state for amido radicals to be  $\Sigma$  which was shown to be an incorrect result due to the neglect of electron-electron repulsion. He pointed out that several populations of orbitals had to be examined in order to find the lowest one if configurational differences were not large. Straightforward application of the "aufbau" principle by which orbitals were filled in a standard manner according to fixed energies was not appropriate in this case.

Using INDO and a systematic population method Koenig calculated three potentials ( $\Sigma_N$ ,  $\Sigma_O$ , and  $\Pi$ ) for the formamido radical that were a function of the CNH angle  $\theta$  (theta). A microwave geometry<sup>57</sup> was assumed for the rest of the molecule.



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It was found that for  $\theta = 115^\circ$  the  $\Pi$  configuration was energetically favored but for  $\theta = 160^\circ$  the  $\Sigma_N$  state, in which the unpaired electron resided in an orbital on nitrogen in the plane of the molecule was lower in energy than for the  $\Pi$  configuration at this angle. The potential curve corresponding to the  $\Sigma_O$  configuration was higher in energy for all  $\theta$  than the other electronic states with a shallow minimum at  $\theta = 105^\circ$ . However, it was felt in this research group that

comparison and ordering of possible electronic states of the formamido radical which differed by only ca. 10 kcal/mol was not unambiguous if an energy minimization with respect to the geometry for each electronic state had not been conducted. Pople and his coworkers<sup>58</sup> had emphasized the importance of such an optimization with respect to the geometry for conformational similar  $C_3H_7^+$  cations using standard self-consistent field molecular orbital theory.

INDO calculations with energy minimization were performed on the N-methylformamido radical as experimental data had been obtained for the N-methylpivalamido radical. Replacement of the tert-butyl group at the carbonyl site was not expected to significantly effect the computed hfsc's and spin densities at the radical center but would reduce the computing costs in limiting the number of heavy atoms. The INDO program was modified in such a manner that the energy converged on a II electronic configuration during the self-consistent field cycles.<sup>59</sup> In this manner the energy minimized structure (as-

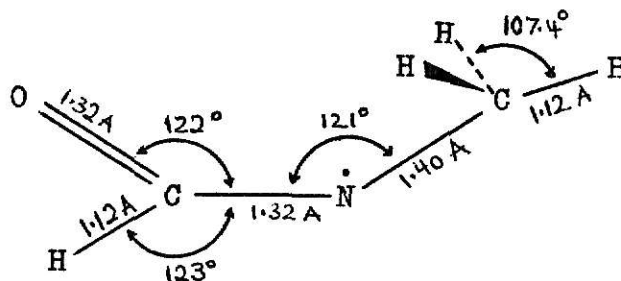


Figure 5. INDO energy-minimized geometry of the N-methylformamido radical in the II electronic configuration.

suming heavy atoms in one plane) for a II N-methylformamido radical was obtained as sketched in Figure 5. The N-methyl group was assumed to be cis to the oxygen atom as the bulky tert-butyl substituent would force the methyl group into this steric arrangement in the reference pivalamido radical. Varying the CNC angle  $\theta$ , an energy function was obtained with a minimum at  $121^\circ$  in both the cis and trans configurations. The highest energy calculated for this electronic state corresponded to a linear geometry at the nitrogen atom ( $\theta = 180^\circ$ ) as shown in Figure 6.

Using the standard INDO program the energy minimized geometry of the N-methylformamido radical in the  $\Sigma_N$  configuration was computed (Figure 7.).

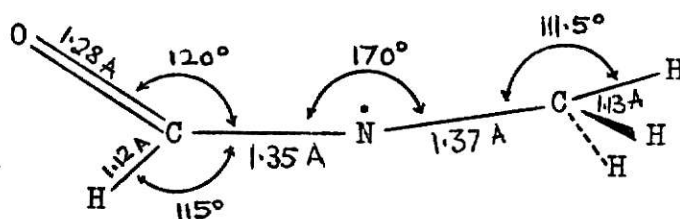


Figure 7. INDO energy-minimized geometry of the N-methylformamido radical in the  $\Sigma_N$  electronic configuration.

Comparison of the two geometries revealed that the electronic configurations mainly effected the CNC bond angle and the heavy atom bond distances. The important calculated parameters from these INDO calculations which were averaged over three methyl rotamers were summarized in Table IV (page 25). As listed in this table the obtained

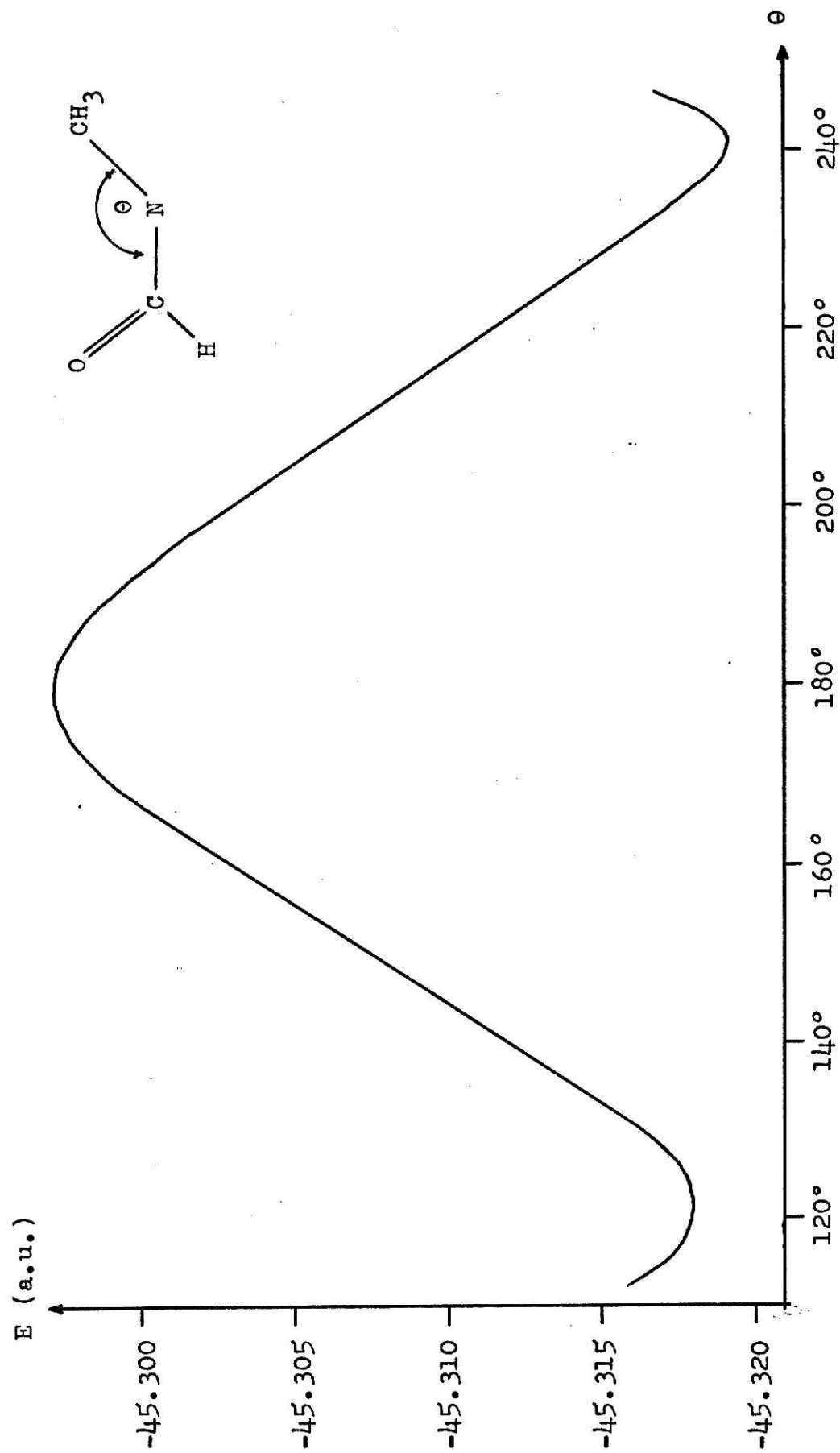


Figure 6. INDO calculated energy of the II N-methylformamido radical as a function of the CNC angle  $\theta$ .

Table IV

INDO Calculated Energies, <sup>a</sup> Spin densities, and Hfsc's <sup>b</sup> for the  
 II and  $\Sigma_N$  Electronic Configurations of the N-Methylformamido

Electronic Configuration	$\theta$	Energy	Spin Densities		$\frac{N}{a}$	$\frac{H}{aHC(O)}$	$\frac{H}{aCH_3}$
			Nitrogen	Oxygen			
II	121°	-45.318665 <sup>c</sup>	0.5476	0.7684	9.28	6.18	18.92
II	180°	-45.296840	0.5394	0.7734	12.20	5.00	18.63
$\Sigma_N$	170°	-45.294283 <sup>c</sup>	0.8162		18.88	33.16	34.52

<sup>a</sup> In atomic units: 1 a.u. = 627.502 kcal/mol

<sup>b</sup> Calculated in gauss

<sup>c</sup> Energy minimized for this electronic configuration  
 All values were averaged over three methyl rotamers.

energy values indicated that the II electronic configuration was favored by 15.31 kcal/mol over the  $\Sigma_N$  configuration when comparing optimized geometries of these two states, but even in the unfavored geometry ( $\theta = 180^\circ$ ) the energy for a II radical was still lower by 1.61 kcal/mol than the energy that had been obtained for a minimized  $\Sigma_N$  configuration. This indicated that for no value of  $\theta$  a crossing of the potentials for the two states occurred, a result that contradicted Koenig's conclusions on the unsubstituted formamido radical.

Comparison of the computed and measured hfsc's of nitrogen and the N-methyl protons gave no conclusive evidence by INDO for a II electronic ground state of amido radicals since the spectral parameters were calculated lower for a II and higher for a  $\Sigma_N$  electronic configuration than observed (cf. Table V). However, it was felt that the INDO method might have overestimated conjugational effects and predicted more extensive delocalization onto the carbonyl group than indeed was occurring. Additionally, Fischer<sup>60</sup> had obtained empirical parameters,  $\Delta(X_i)$ , from esr studies describing the ability of a substituent to remove spin density from a carbon-centered radical. A value of 0.162 was listed for the carbonyl group indicating that it was effective in reducing the spin density from an adjacent radical center by only 16.2%. In order to obtain an estimate of the effect of a carbonyl group adjacent to a carbon radical center as calculated by the INDO method computations were performed on the 2-propionaldehyde radical, a II radical. The heavy atom distances were optimized with respect to the energy but Pople's

standard geometrical model "A" was used for the remaining bond distances and angles.

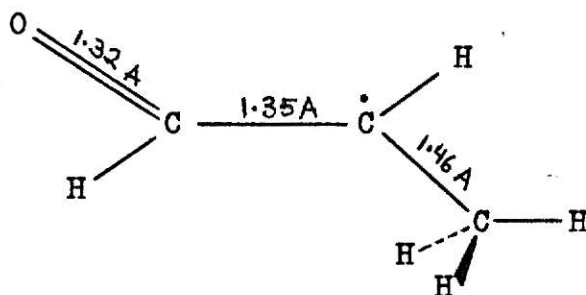


Figure 8. Partial INDO energy-minimized geometry of the 2-propionaldehyde radical.

The computed data along with experimental values obtained by Russell and Lokensgard<sup>43</sup> for an  $\alpha$ -keto radical were summarized in Table V. For the carbon-centered radicals it was found that INDO overestimated the effect of the carbonyl group to delocalize the unpaired electron and calculated the hfsc for the methyl protons 29% lower than experimentally observed. Extrapolating these results to the amido radicals it seemed likely that hfsc's for the N-methyl protons would also be calculated too low. Smaller calculated spectral parameters had only been obtained for the II electronic configuration (second and third entry in Table V). Indeed, the energy-minimized II configuration predicted the methyl protons hfsc to be 35% lower than experimentally observed which was similar to the difference between calculated and observed hfsc's for the  $\alpha$ -keto case. It was there-

Table V

Comparison of Observed and INDO Calculated Hfsc's<sup>a</sup> andSpin Densities of Amido and  $\alpha$ -Keto Radicals

Radical	Spin Density <sup>b</sup>	$\frac{N}{a}$	$\frac{aCH_3}{H^C}$	Method
$(CH_3)_3CC(O)\dot{N}CH_3$		15.00	29.30	Experimental <sup>d</sup>
$HC(O)\dot{N}CH_3$ (II, $\theta = 121^\circ$ )	0.5476	9.28	18.92	INDO
$HC(O)\dot{N}CH_3$ (II, $\theta = 180^\circ$ )	0.5394	12.20	18.63	"
$HC(O)\dot{N}CH_3$ ( $\Sigma_N$ , $\theta = 170^\circ$ )	0.8162	18.88	34.52	"
$CH_3C(O)\dot{C}HCH_3$	0.77		22.6	Experimental <sup>e</sup>
$HC(O)\dot{C}HCH_3$	0.3975		16.00	INDO

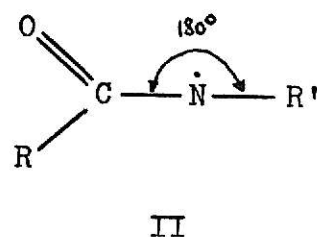
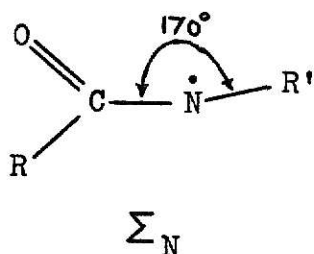
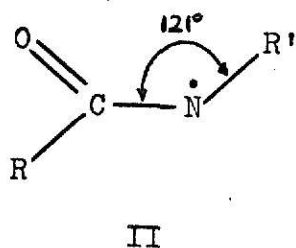
<sup>a</sup> Reported in gauss<sup>b</sup> Spin density on nitrogen (on carbon for last two entries)<sup>c</sup> Interaction with three methyl hydrogens adjacent to the radical center<sup>d</sup> This work<sup>e</sup> Reference 43

Computed parameters were averaged over three methyl rotamers.

fore concluded that the INDO method favored a II electronic structure for amido radicals but failed to predict correct spin densities and hfsc's for such a configuration due to the overestimate of conjugational effects with the carbonyl group.

## 5. Conformational Preferences of Amido Radicals

The preceeding INDO calculations on the N-methylformamido radical indicated a dependence of the electronic configuration on the relevant angle at the nitrogen radical center. For a linear or almost linear alignment of substituents the energies of the II and  $\Sigma_N$  were calculated to be very close but a pronounced energetical preference of 15.31 kcal/mol was given to a bent structure 14.



$$\Delta E_{14+15} = 15.31 \text{ kcal/mol}; \Delta E_{15+16} = -1.61 \text{ kcal/mol}$$

14

15

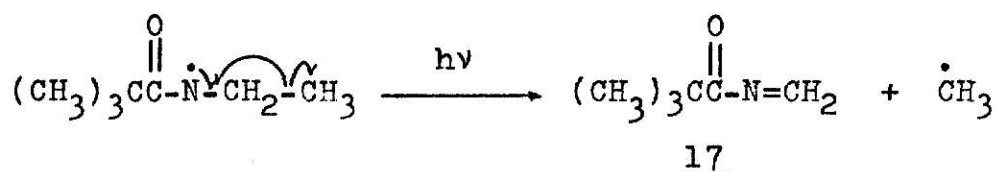
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An investigation of the conformation of amido radicals would reveal further insight in the electronic structure since a bent geometry ( $\theta = 121^\circ$ ) would unambiguously indicate a II electronic ground state as predicted by the INDO method. As vibrational relaxation times were short compared with the time scale of the esr experiment only vi-

brational ground state geometries had to be considered.<sup>61</sup> It had been pointed out in this research group that analysis of the  $\beta$ -hydrogen hyperfine interaction revealed decided conformational preferences in the dialkylamino radicals and dialkylaminium radical cations.<sup>31,36</sup> The magnitudes of the  $\beta$ -hydrogen hyperfine coupling constants were found to be quite different with the diethyl substituted radicals exhibiting a significant larger interaction than the dimethyl substituted species whereas the coupling in the diisopropyl radicals was considerably smaller. From the magnitude of the  $\beta$ -hydrogen coupling constant it was possible to estimate the angle between the C-H bond and the axis of the p orbital containing the unpaired electron for the time-averaged conformations of the diethylamino and diisopropyl substituted radicals which was found to be  $35^\circ$  and  $60^\circ$ , respectively. From the examination of molecular models it was found that the decided conformational preferences arose from steric interactions of the alkyl groups. A smaller deviation from the coupling constants of the freely rotating methyl group was found in the charged radicals indicating a lower barrier to rotation. INDO energy-minimized structures indicated a CNC angle of  $117^\circ$  for the dimethylamino radical and a  $9^\circ$  larger CNC angle for the dimethylaminium radical cation allowing for greater ease of rotation.

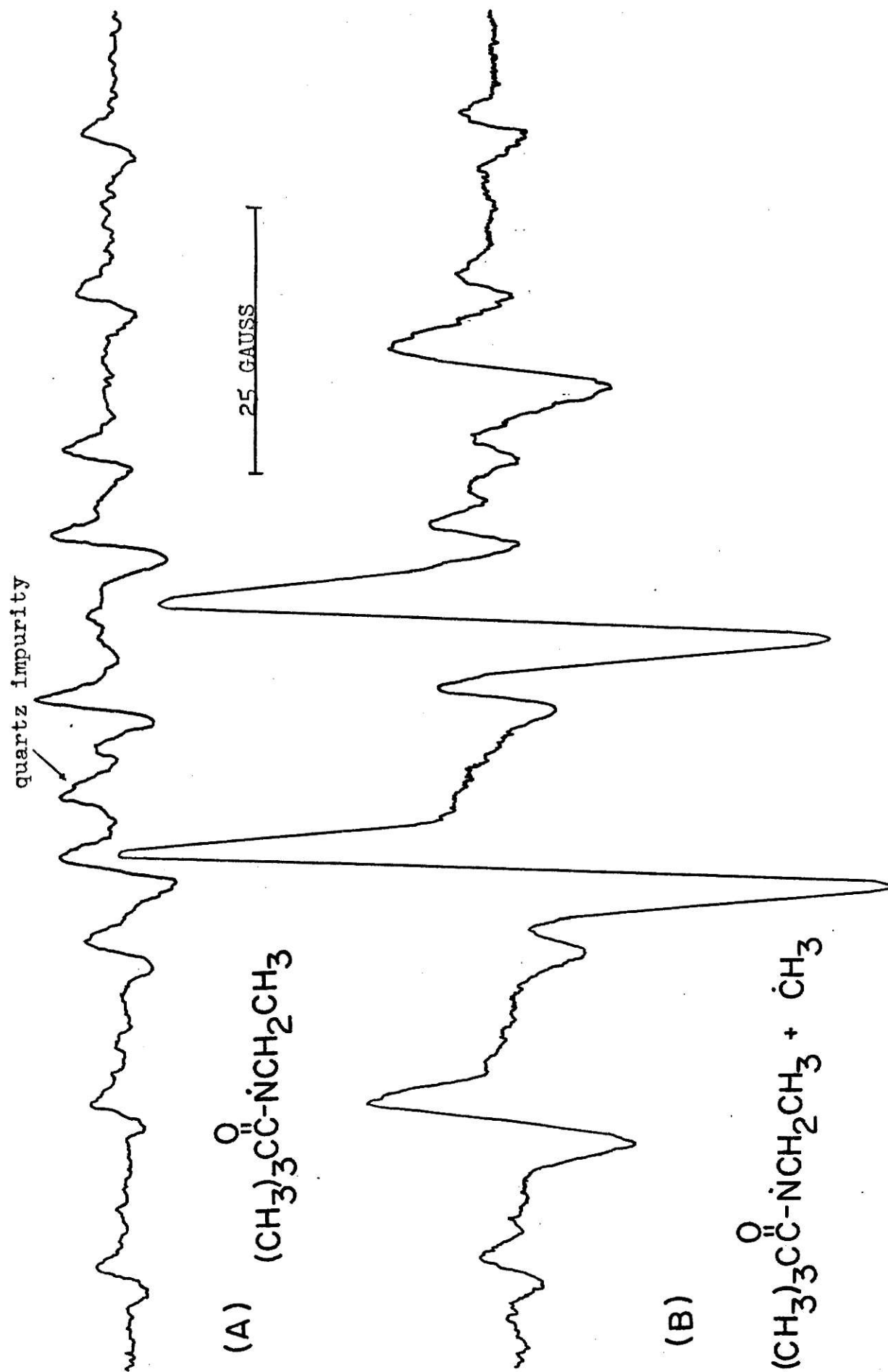
It was therefore expected that a similar dependence of the  $\beta$ -hydrogen hyperfine interaction on the alkyl substitution in amido radicals would be indicative of a bent geometry at the nitrogen radical center since no significant barrier to rotation in the N-ethyl- and N-iso-propylamido radicals was expected for a linear CNC geometry.

N-Chloro-N-ethylpivalamide and N-chloro-N-iso-propylamide were synthesized in the previously described manner. Upon uv irradiation (2000 W mercury lamp) of degassed solutions of these amides in cyclopropane spectra of the corresponding amido radicals were obtained. The esr spectrum assigned to the N-ethylpivalamido radical (Figure 9 A) featured a large 1:2:1 triplet due to the  $\beta$ -methylene protons each line split into a smaller 1:1:1 triplet from hyperfine interaction with the nitrogen nucleus. The poor signal to noise ratio in the spectrum was attributed to the instability of this radical towards elimination of a methyl radical, the spectrum of which ( $a^H = 21.0$  G,  $g = 2.0026$ )<sup>62</sup> appeared after several minutes of irradiation of the parent N-chloroamide as shown in Figure 9 B: the 1:3:3:1 quartet due to the methyl radical dominated the spectrum but features of the spectrum of the N-ethylamido radical were still apparent. A similar  $\beta$ -elimination had been observed during the photolysis of ethyl-N-methoxycarbamate,  $C_2H_5OC(O)NHCH_3$ , to form the carboethoxymethyl nitroxide,  $C_2H_5OC(O)N(\dot{O})CH_3$ .<sup>41</sup> In the present case, however, there was no evidence that the eliminated methyl radical attacked the substrate which was most likely an imine (17).



The spectrum assigned to the N-iso-propylpivalamido radical (Figure 10) showed six broad absorption lines of equal intensity distribu-

Figure 9. Electron spin resonance spectrum of (A) the N-ethylpivalamido radical and (B) the methyl radical appearing after prolonged uv irradiation.



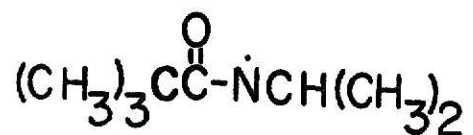
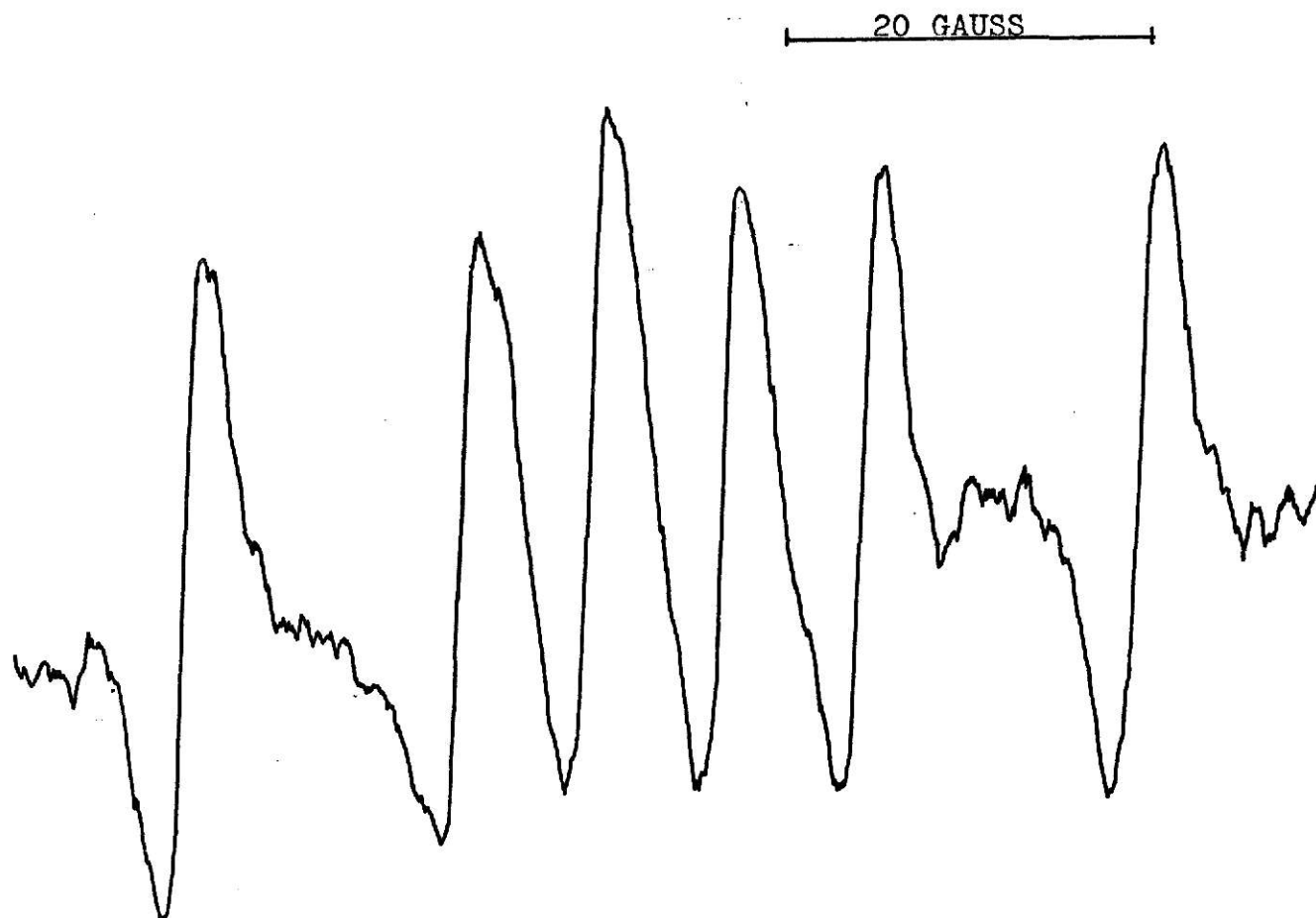


Figure 10. Electron spin resonance spectrum of the N-iso-propylpival-amido radical.

tion which was interpreted in terms of a 1:1 doublet from hyperfine interaction with the methine proton of the iso-propyl group, each line split into a smaller 1:1:1 triplet due to the nitrogen nucleus. The spectral parameters of both amido radicals were summarized in Table VI.

Table VI  
Spectral Parameters<sup>a</sup> of the N-Ethyl- and  
N-iso-Propylpivalamido Radicals

Radical	$a^N$	$a^H_\beta$	$g \text{ value}^c$	Temp., C
$(CH_3)_3CC(O)\dot{N}C_2H_5$	$14.7^b$	$37.8^b$	2.0053	-100
$(CH_3)_3CC(O)\dot{N}CH(CH_3)_2$	14.85	22.10	2.0053	-100

<sup>a</sup> Reported in gauss, estimated accuracy  $\pm 1\%$  except where noted

<sup>b</sup> Estimated accuracy  $\pm 3\%$  due to poor signal to noise ratio

<sup>c</sup> Corrected to second order, estimated accuracy  $\pm 0.0001$

Comparison of the  $\beta$ -hydrogen coupling constants of these two amido radicals with the corresponding values obtained for dialkylamino radicals and dialkylaminium radical cations revealed a similar dependence of the magnitude of the  $\beta$ -hydrogen hyperfine interaction upon alkyl substitution at the nitrogen site (Table VII). This dependence was found to be very close to the behavior exhibited by the dialkylamino radicals (first column in Table VII) and suggested that the

Table VII

Comparison of  $\beta$ -Hydrogen Hfsc's<sup>a</sup> of Related  
Nitrogen-Centered II Radicals

Substituent Group R	Radical- $\beta$ -Hfsc's		
	$\text{R}_2\text{N}^{\cdot\text{b}}$	$\text{R}_2\text{NH}^{\cdot\text{c}}$	$(\text{CH}_3)_3\text{CC}(\text{O})\text{NR}^{\cdot\text{d}}$
$\text{CH}_3$	27.36	34.27	29.30
$\text{C}_2\text{H}_5$	36.90	37.19	37.8
$\text{CH}(\text{CH}_3)_2$	14.31	32.41	22.10

<sup>a</sup> Reported in gauss

<sup>b</sup> Reference 31, spectra obtained at  $-90^\circ$

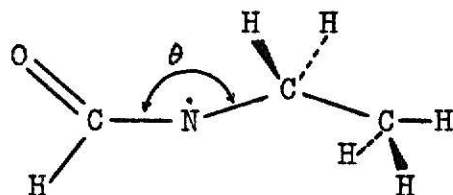
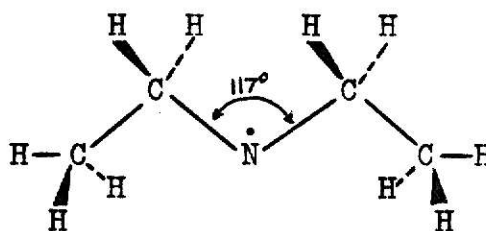
<sup>c</sup> Reference 36, spectra obtained at  $31^\circ$

<sup>d</sup> This work, spectra obtained at  $-100^\circ$

preferred conformation at the nitrogen site in amido radicals was also bent. This was taken as further evidence for a II electronic ground state configuration since the INDO method predicted an angle of  $121^\circ$  for the energy-minimized geometry of amido radicals.<sup>63</sup>

The semiempirical INDO method was expected to give reasonable estimates of rotational barriers of interest here. For example, the INDO method estimated a rotational barrier of 2.20 to 2.25 kcal/mol (depending on the geometry) for ethane which compared well with the experimental value of 2.875 kcal/mol.<sup>64</sup> INDO calculations were performed on three different rotamers of the N-ethylformamido radical (18) in the II and  $\Sigma_N$  electronic configuration ( $\theta = 121^\circ$  and  $170^\circ$ , respectively) utilizing the standard model "A" for the ethyl

group and the minimized geometric parameters for the remaining bond distances and angles (cf. Figures 5 and 7). Additional calculations were performed on the diethylamino radical (19) for comparison purposes using the same data for the ethyl group and minimized parameters obtained previously for the CNC bond angle and the carbon-nitrogen bond distances in the dimethylamino radical.<sup>36</sup>

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Three conformations obtained by rotation ( $0^\circ$ ,  $90^\circ$ , and  $180^\circ$ ) about the nitrogen-methylene carbon bond were considered, the structures 18 and 19 describing the  $0^\circ$  geometry. The energy differences calculated by INDO for the three rotamers were taken relative to the energy computed for the preferred conformation of each radical species as summarized in Table VIII.

As anticipated the barrier to rotation was calculated to be higher for the N-ethylformamido radical in the  $\Pi$  electronic configuration than in the  $\Sigma_N$  state although the energy difference of 2.42 kcal/mol between the unfavored conformations was less than expected since no important steric interactions seemed possible in the  $\Sigma_N$  configuration due to the opened geometry ( $\theta = 170^\circ$ ). However,

Table VIII

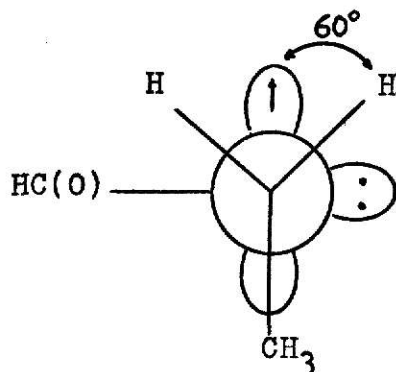
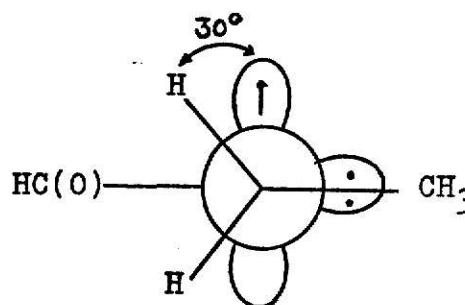
Relative Energy Differences<sup>a</sup> for Ethyl Rotamers of the N-Ethyl-formamido and Diethylamino Radicals as Calculated by INDO

Radical	Energy Differences		
	0°	90°	180°
HC(O) $\dot{\text{N}}$ -C <sub>2</sub> H <sub>5</sub> (II)	3.14	0.0	7.29
HC(O) $\dot{\text{N}}$ -C <sub>2</sub> H <sub>5</sub> ( $\Sigma_{\text{N}}$ )	0.48	4.87	0.0
C <sub>2</sub> H <sub>5</sub> - $\dot{\text{N}}$ -C <sub>2</sub> H <sub>5</sub> (II)	2.58	0.0	6.53

<sup>a</sup> Reported in kcal/mol

the potential obtained for the II amido radical was similar to the one calculated for the diethylamino radical in agreement with previous conclusions based on  $\beta$ -hydrogen hyperfine interactions as determined by esr. The fact that significant energy differences were calculated for the amido radical in the  $\Sigma_{\text{N}}$  electronic configuration indicated that considerable electronic effects were operating. It had been shown from results of INDO calculations that, in general, carbon-carbon hyperconjugation was more favorable than carbon-hydrogen hyperconjugation in cationic species while the reverse was true for carbanions which could be compared to nitrogen with its lone pair of electrons. As preferred conformations in the present case were predicted by INDO when the carbon-carbon bond in the ethyl group eclipsed the spin bearing orbital on nitrogen (90° rotamer for II and

180° rotamer for  $\sum_N$  radicals as indicated in structure 20) it was concluded that the lone pair of electrons on nitrogen had a decided influence on the conformation since the lone pair - methylgroup interactions were minimized in conformation 20 and C-H - lone pair and

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C-CH<sub>3</sub> - unpaired electron interactions were maximized. But it was experimentally observed that the  $\beta$ -hydrogen interaction increased when changing the substituent group from methyl to ethyl (cf. Table VII) indicating that the  $\beta$ -protons were in closer proximity to the spin bearing orbital on the time-average in the ethyl group than in the freely rotating methyl group. Thus structure 21 would more likely represent the preferred conformation of the N-ethylformamido radical accounting for the experimental results.

It was therefore concluded that the INDO method failed to predict correct conformational preferences due to the overestimate of hyperconjugational effects with the unpaired electron. The potential barriers to rotation calculated to be of the order of several

kcal/mol seemed unlikely, too. Both Fessenden<sup>66</sup> and Krusic and Kochi<sup>67</sup> found from esr studies that simple acyclic hydrocarbon radicals exhibited potential barriers to rotation of ca. 0.3 kcal/mol.

## 6. Investigation of Cyclic N-Chloroamides

A more conclusive evidence for the effect of the CNC angle upon the electronic ground state in amido radicals was expected from an investigation of cyclic radicals since the ring structure would lock the angle  $\theta$  at the nitrogen atom at a certain value. If variation of the ring size had a decided influence on the esr spectral parameters insight of a change in the electronic configuration could be deduced. Symons<sup>44</sup> had pointed out that for example in diacylamino radicals a change from a  $\Pi$  to a  $\Sigma$  electronic configuration might be induced by a suitable choice of substituent groups or by a constraint on the relevant bond angle, e.g. comparing open chain and cyclic radicals. Additionally, results based on the  $\beta$ -hydrogen hyperfine interaction in the acyclic species could be confirmed if similar spectral parameters were obtained for cyclic amido radicals.

Upon photolysis (2000 W mercury lamp) of N-chloro- $\epsilon$ -caprolactam (seven membered ring) and N-chloro-2-pyrrolidinone (five membered ring) in degassed solutions of cyclopropane at low temperatures no esr spectra could be recorded, results possibly attributable to poor solubility of these N-chlorolactams at low temperatures. Therefore some methyl substituted 2-pyrrolidinones were synthesized following the synthetic route given by Moffett and White<sup>68</sup> as shown in Figure 11. The two methyl groups in the 5-position were expected not only

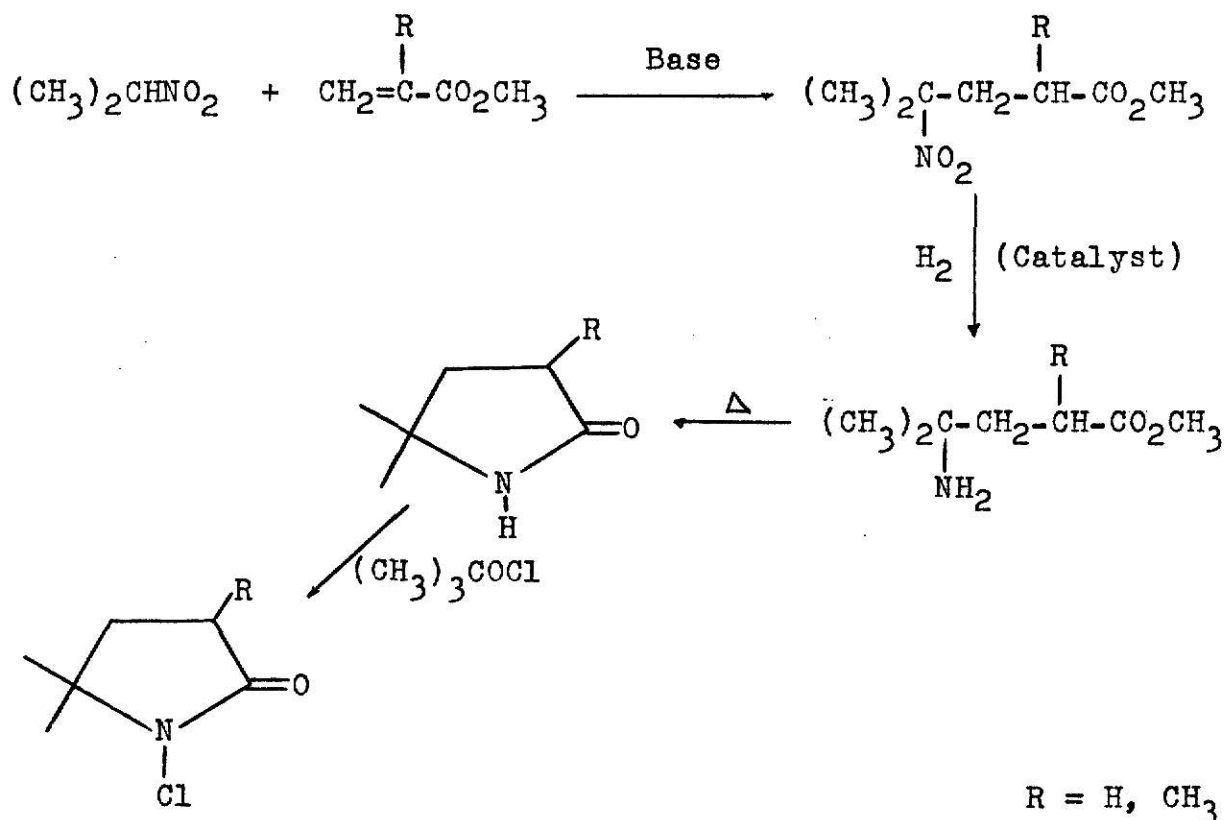
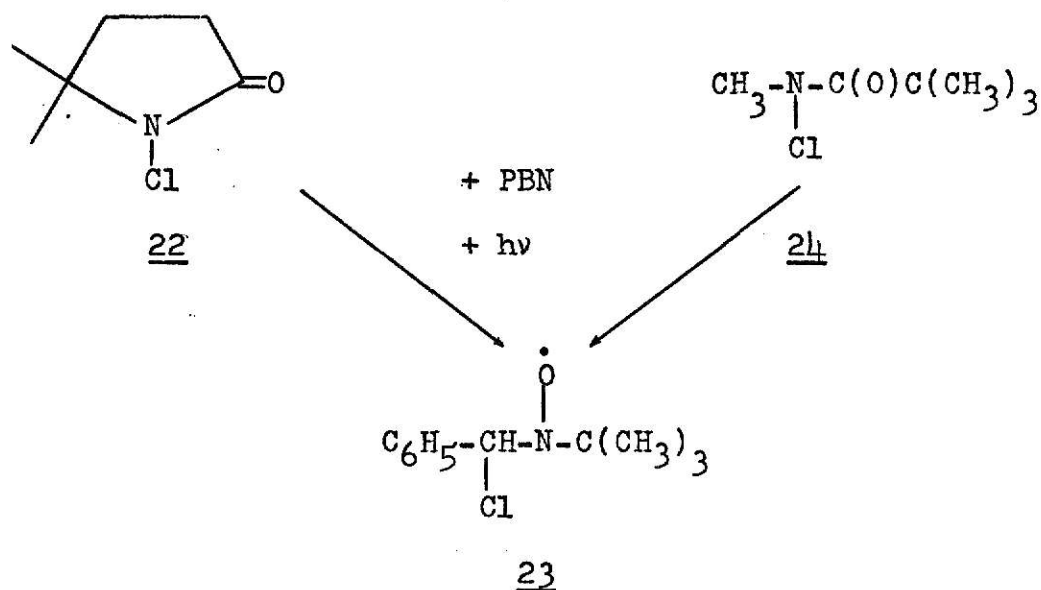


Figure 11. Syntheses of methyl substituted N-chloro-2-pyrrolidones.

to improve the solubility due to the asymmetry introduced but also to stabilize a possible nitrogen-centered radical since the acyclic N-tert-butylacetamido radical had been shown to be relatively stable. However, no signals attributable to the expected amido radicals were detected upon irradiation of these N-chlorolactams.

If very transient radicals were produced by uv irradiation of N-chlorolactams photolysis in the presence of a suitable compound could trap these species. The simplest spin trapping reagent that

proved useful in the case of the N-methylacetamido radical was molecular oxygen. However, under similar experimental conditions no spectra of nitroxides could be recorded. An alternate trapping reagent appeared to be phenyl-tert-butyl nitrone (PBN) as the nitroxides resulting from spin trapping reactions had been shown to be relatively stable.<sup>69</sup> Photolysis of N-chloro-5,5-dimethyl-2-pyrrolidinone (22) in a degassed benzene solution at room temperature yielded strong, well resolved esr signals that were assigned to the  $\alpha$ -chlorobenzyl-tert-butyl nitroxide (23) by comparison with data published by Janzen, et al.<sup>70</sup>



As the same spectrum was obtained upon photolysis of N-chloro-N-methylpivalamide in the presence of PBN it was concluded that in both cases a homolytic cleavage of the N-Cl bond occurred, followed by the reaction of the chlorine atom with the nitrone to yield the

stable  $\alpha$ -chloroalkyl nitroxide. These trapping reactions established that the formation of a chlorine atom and an amido radical was probably the initial photolytic reaction. Whereas it was possible to observe the N-methylpivalamido radical an esr spectrum corresponding to a cyclic amido radical was not recorded indicating that further rapid reactions in the latter case were possibly accounting for the insufficient steady-state concentration of cyclic amido radicals.

The previously employed technique by Wood and Lloyd<sup>46-48</sup> using an adamantane matrix seemed suitable for providing some insight into possible secondary reactions of cyclic amido radicals since no solvent abstraction or other intermolecular reactions would be possible. X-irradiation of trapped N-chlorolactams in the adamantane matrix at liquid nitrogen temperatures produced isotropic esr signals after the sample was warmed to room temperature. In this manner spectra were recorded from N-chloro- $\epsilon$ -caprolactam, N-chloro-2-pyrrolidinone, and the 5,5-dimethyl substituted analogue of the latter lactam. An interpretation of these spectra was complicated by an intense quartz signal resulting from radiation damage in the sample tube itself. A 1:1:2:2:1:1 splitting pattern seemed common to all spectra although broad absorption lines complicated the assignment of intensity ratios as could be appreciated from the spectrum obtained from N-chloro- $\epsilon$ -caprolactam (Figure 12). This spectrum featured a large quartet (with intensity ratios of 1:2:2:1 or possibly 1:3:3:1) of 18.9 G each line split into a smaller 1:1 doublet of 6.1 G. The observed g values of 2.0028, 2.0034, and 2.0037 for the radicals derived from

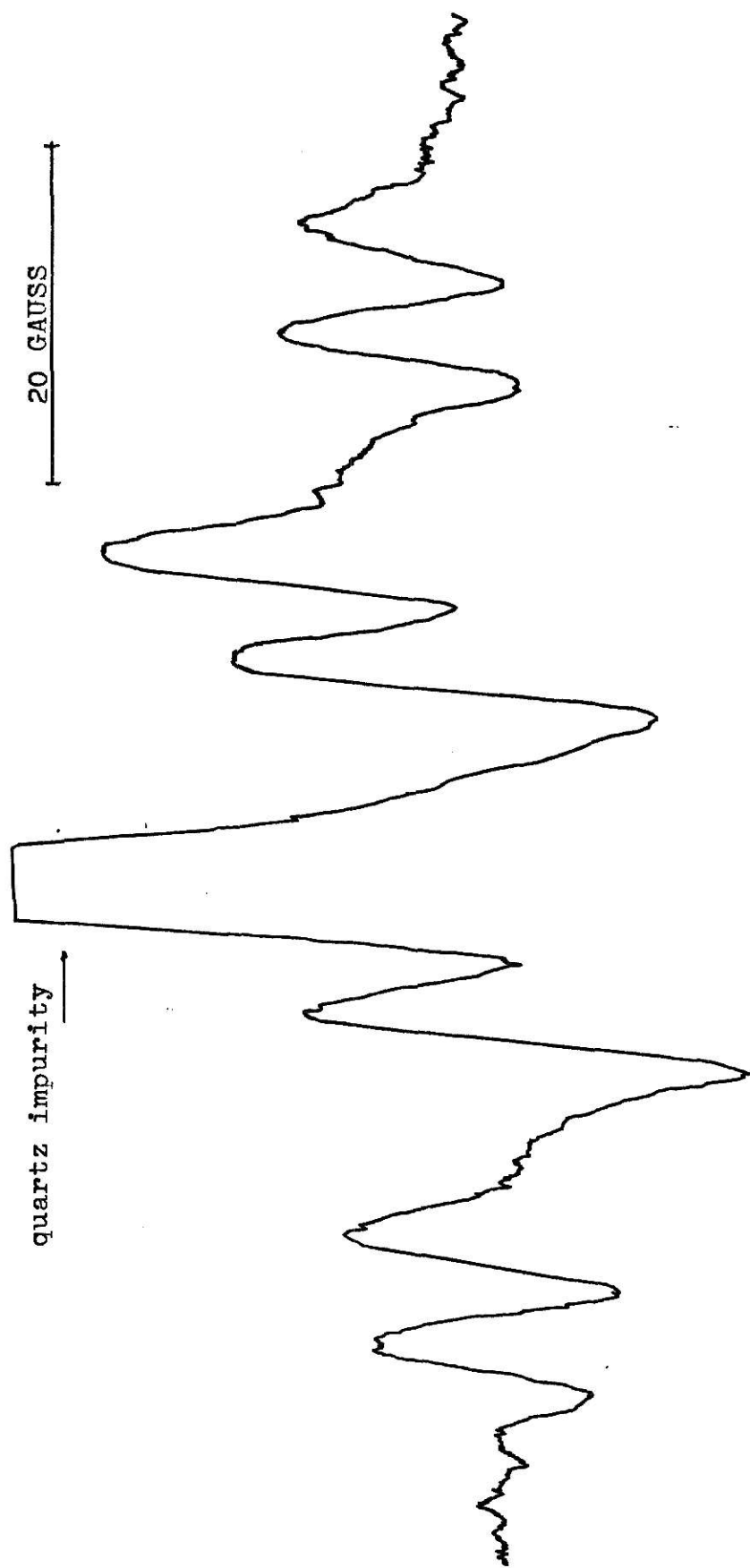
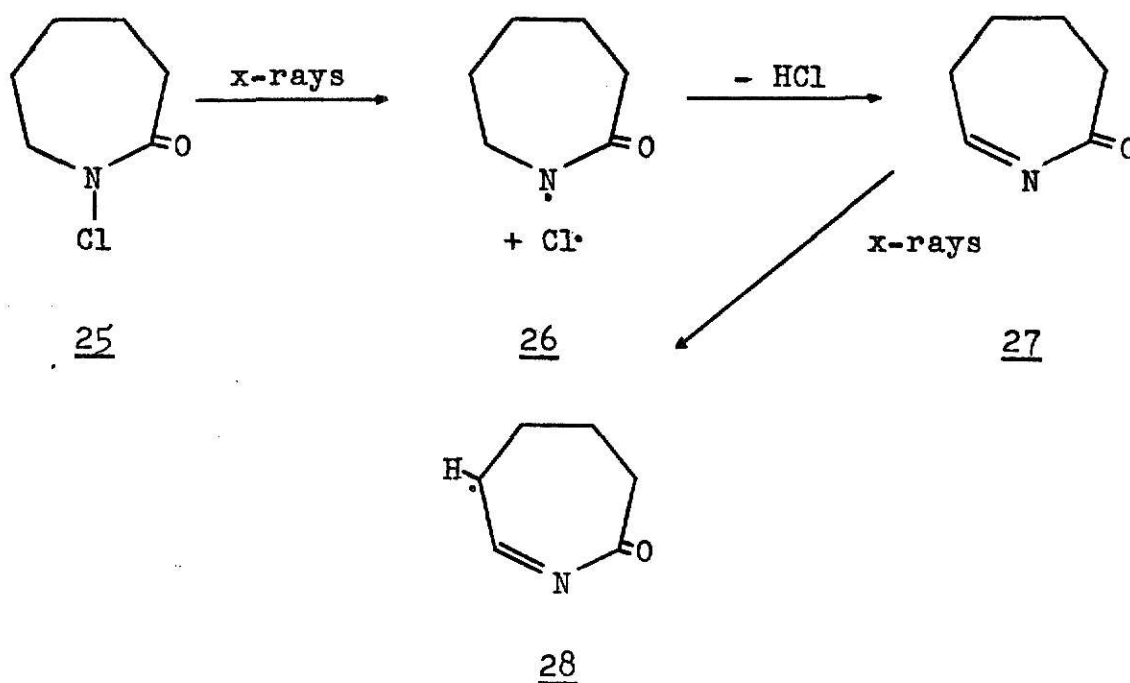


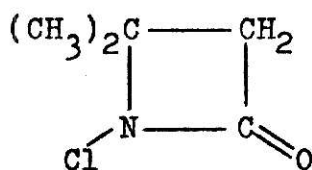
Figure 12. Electron spin resonance spectrum derived from N-chloro-ε-caprolactam in an adamantane matrix upon x-irradiation.

N-chloro-ε-caprolactam, N-chloro-2-pyrrolidinone, and N-chloro-5,5-dimethyl-2-pyrrolidinone, respectively were significantly smaller than the values obtained for acyclic amido radicals (2.0044 and 2.0053) indicating that different radical species were observed in these cases. The lower g values for the cyclic species suggested carbon-centered II radicals.<sup>62</sup>



As no spectra were recorded using the lactams in the adamantane matrix an abstraction reaction of a  $\beta$ -hydrogen by a chlorine atom formed upon cleavage of the N-Cl bond seemed a possible reaction pathway leading to the formation of a cyclic imine (structure 27 for the seven membered ring case) followed by loss of an allylic hydrogen caused by radiation damage to form the carbon-centered radical (28).

If x-irradiation in an adamantane matrix led to the formation of a cyclic imine it was anticipated that such a reaction pathway should be unlikely for N-chloro- $\beta$ -lactams as the introduction of a double bond would lead to considerable strain increase in the four membered ring. However, no esr spectrum could be recorded either in solution or in an adamantane matrix upon irradiation of N-chloro- $\beta$ -iso-valerolactam (29).



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A trapping reaction with PBN yielded the same spectrum that had been obtained previously and was assigned to the  $\alpha$ -chlorobenzyl-tert-butyl nitroxide (23) indicating that an initial N-Cl bond cleavage also occurred in this case. As no radicals were detected using the matrix technique, different radiation damage reactions were available for this strained ring compound. For example, N-chloro- and N-bromo- $\beta$ -lactams were known to undergo peroxide-induced rearrangement reactions to the corresponding isocyanate in the presence of a cocatalyst, generally an olefin.<sup>71</sup>

Hudson and Jackson<sup>72</sup> and later Kochi and Edge<sup>73</sup> generated carbon-centered radicals from haloalkyl compounds and photochemically generated triethylsilyl radicals in cyclopropane. However, application of this technique to cyclic and acyclic amides did not prove fruitful since triethylsilane reacted very vigorously with both N-

chloro- and N-bromoamides upon mixing even at reduced temperatures. Additionally, upon photolysis of samples made up at liquid nitrogen temperatures no esr signals could be recorded.

Thus it was not possible to observe cyclic amido radicals under different experimental conditions employed; the spectra obtained, although an unequivocal assignment was not possible, indicated that fast secondary reactions which could include abstraction, elimination or ring opening occurred after the initial formation of a nitrogen-centered radical, the electronic ground state configuration of which remained speculative. Some later results with sulfonamido radicals gave evidence for the conclusion that cyclic and acyclic radicals have the same electronic configuration.

## II. PART II: TRANSIENT SULFONAMIDO FREE RADICALS

### A. Introduction

Sulfonamides,  $R-SO_2-NHR'$  ( $R, R' = \text{alkyl or aryl}$ ) were structurally similar to the corresponding carboxyamides,  $R-CO-NHR'$ , yet were known to differ in their reactivity. For example, the sulfonyl group ( $-SO_2-$ ) exhibited a more pronounced effect on reducing the basicity of the adjacent nitrogen atom than the carbonyl group ( $-CO-$ ). On the other hand, sulfonamido radicals,  $R-SO_2-\dot{N}-R'$ , like amido radicals had been claimed as intermediates in some photochemical reactions.

Generally, N-halosulfonamides,  $R-SO_2-N(Hal)-R'$  ( $Hal = Cl \text{ or } Br$ ), were used as possible sources of sulfonamido radicals in free radical reactions. Fuller and Hickinbottom<sup>74</sup> reported that N-chlorosulfonamides could be used as chlorinating agents for the peroxide induced chlorination of n-alkanes. They offered a reaction scheme in which a proposed sulfonamido radical functioned as the chain carrier. Of more importance, however, for synthetic organic chemistry were rearrangement reactions observed upon photolysis of N-chloro-N-alkylsulfonamides that were analogous to the ones reported for N-chloroamides.<sup>1-5</sup> Verma and Srivastava<sup>75</sup> showed that N-(p-chlorophenyl)- and N-pyrrolidinosulfonamides were produced upon irradiation of N-chloro-N-phenyl- and N-chloro-N-n-butylsulfonamides, respectively. The products formed were best being accounted for by assuming a Hoffmann-Loeffler type free radical reaction mechanism. Okahara and his coworkers<sup>76</sup> found that the photorearrangement of N-chloro-N-alkyl-n-alkanesulfonamides led to the formation of  $\gamma$ - and  $\delta$ -chloroalkane-

sulfonamides. This was of some importance as subsequent alkali treatment of the rearranged products opened a convenient route towards the synthesis of cyclic sulfonamides (or sultams) which received attention in the field of polymer chemistry as starting materials for the preparation of polysulfonamides.<sup>77</sup> A similar method for the synthesis of N-alkylsultams was reported by Neale and Marcus<sup>78</sup> who postulated a reaction path involving sulfonamido radicals as intermediates in these rearrangement reactions.

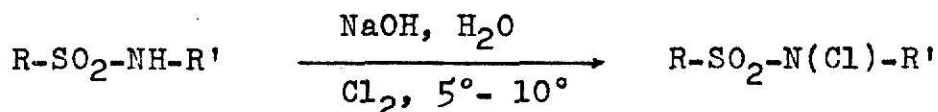
Based on these product studies it was of interest to establish unambiguously the existence of sulfonamido radicals by electron spin resonance spectroscopy. Information about their electronic structure could then be deduced from the observed spectral parameters as had been discussed in the introduction of Part I. From the similarities mentioned above it was expected that sulfonamido radicals would have hfsc's of the same order of magnitude as the corresponding amido radicals which would also imply a II electronic structure. Furthermore, comparison of esr spectral data of the two radical species should yield some insight in the electronic effects of the carbonyl vs. the sulfonyl group.

## B. Discussion of Results

### 1. Generation and Identification of Sulfonamido Radicals

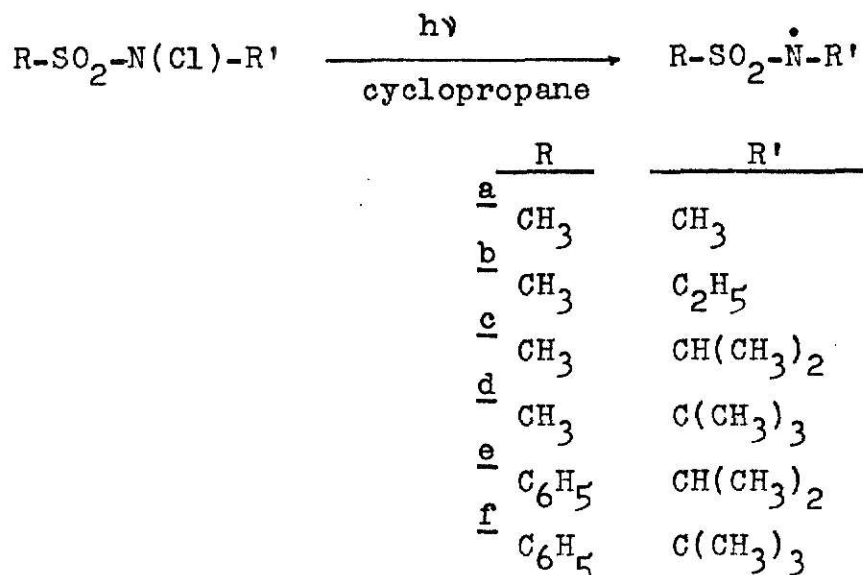
Based on the results reported in Part I for amido radicals it was anticipated that upon photolysis of N-chloro-N-alkylsulfonamides

in cyclopropane directly in the cavity of the esr spectrometer signals of the corresponding sulfonamides should be detected. The preparation of the N-chloro compounds from the corresponding N-alkylsulfonamides was achieved in good yields by the method of Okahara and his coworkers<sup>76</sup> by passing chlorine into a suspension of the sulfonamide in an aqueous sodium hydroxide solution at ice bath temperatures.



Using tert-butylhypochlorite as a chlorinating agent<sup>78</sup> required much longer reaction times and was only applied in two cases (see experimental section).

In this manner several N-chloro-N-alkylmethane- and phenylsulfonamides were prepared and degassed solutions of these amides in cyclopropane (ca. 10 - 20% by volume) were photolyzed at different temperatures.



The esr spectra produced showed the same basic patterns as the ones obtained from photolysis of N-chloroamides in solution and were therefore assigned to the corresponding N-alkylsulfonamido radicals. The sulfonamido radicals generated in this manner showed an enhanced stability compared to the corresponding amido radicals and spectra were generally recorded at higher temperatures ( $-20^{\circ}$  to  $+30^{\circ}$ ) which largely increased the solubility of the N-chlorosulfonamides in cyclopropane. But even at these temperatures it was not possible to obtain spectra of the phenyl analogs of a and b due to insolubility in a variety of low-dielectric solvents. Analysis of the spectra obtained was straightforward and unequivocally established the location of the unpaired electron on the nitrogen nucleus. The spectra featured nitrogen hfsc's of ca. 1.5 to 2 G smaller than the values obtained for the corresponding amido radicals but g values and  $\beta$ -hydrogen hfsc, with the exception of the N-iso-propyl derivatives, of the same order of magnitude. The spectrum assigned to the N-methylmethanesulfonamido radical,  $\text{CH}_3\text{-SO}_2\text{-}\dot{\text{N}}\text{-CH}_3$ , as shown in Figure 13 featured a large 1:3:3:1 quartet due to the N-methyl protons each line split into a smaller 1:1:1 triplet from hyperfine interaction with the nitrogen nucleus. As the nitrogen hfsc was less than half the  $\beta$ -hydrogen hfsc the spectral lines did not overlap as in the case of the N-methylpivalamido radical (Figure 1). The spectrum assigned to the N-ethylmethanesulfonamido radical (Figure 14) showed similar coupling patterns as the N-ethyl substituted amido radical. However, no  $\beta$ -elimination was detectable in the present case indicating an enhanced stability of the sulfonamido radicals towards secondary reactions.

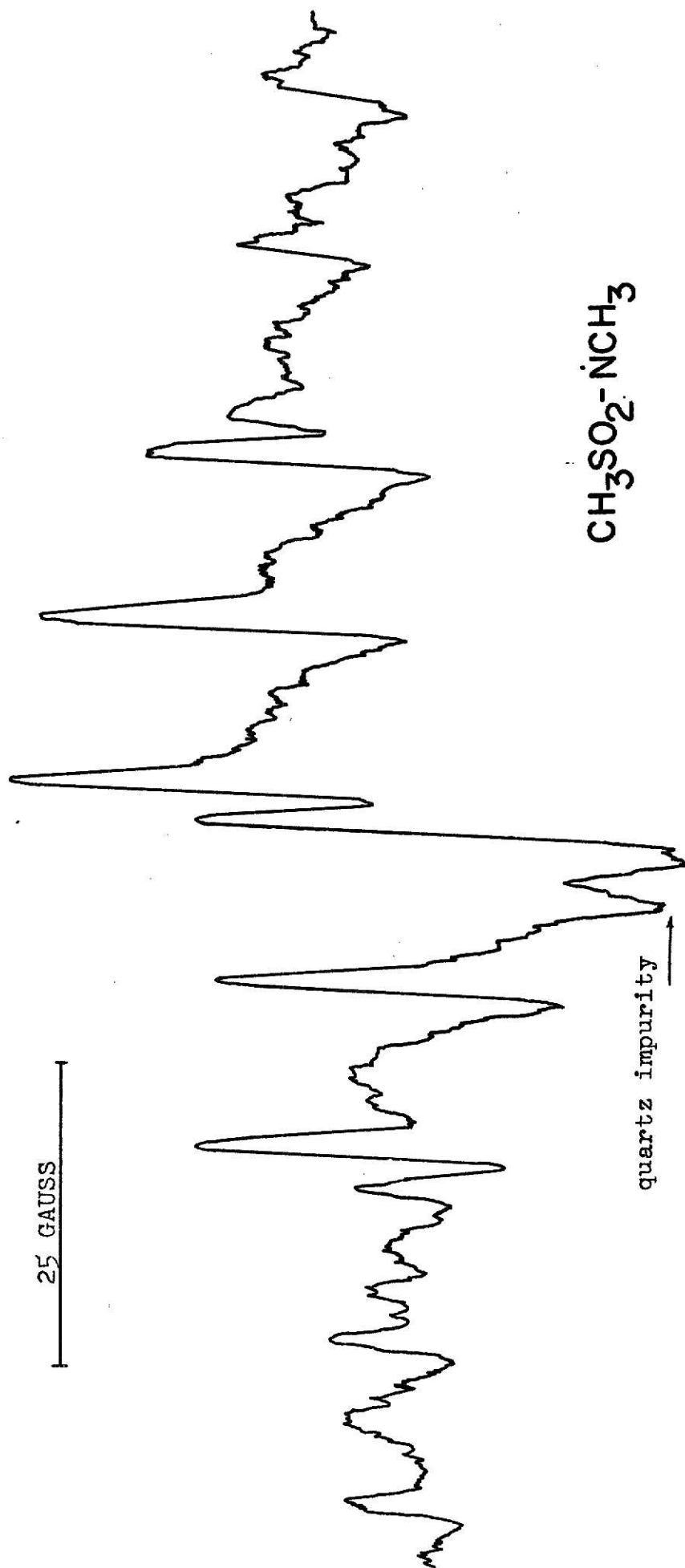


Figure 13. Electron spin resonance spectrum of the N-methylmethanesulfonamido radical.

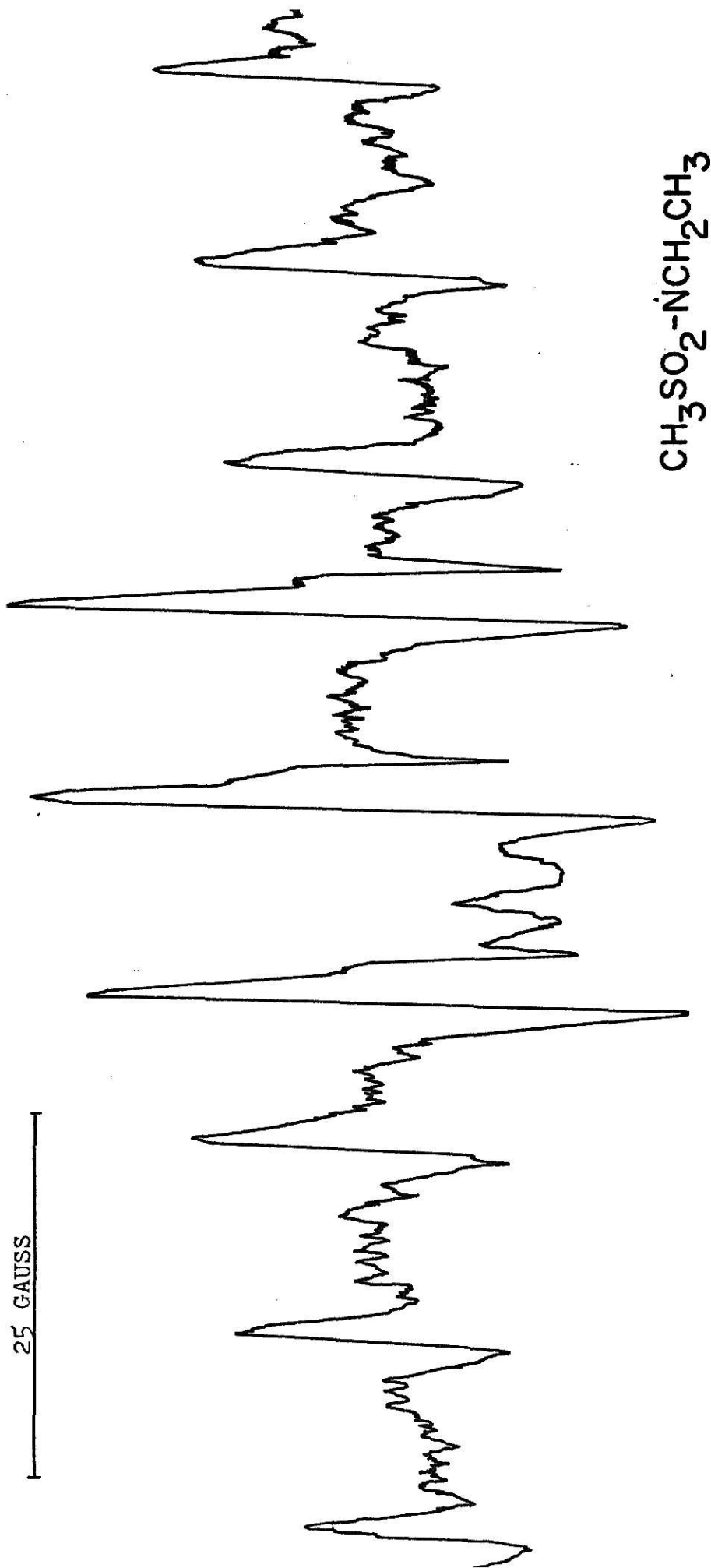


Figure 14. Electron spin resonance spectrum of the N-ethylmethanesulfonamido radical.

10 GAUSS

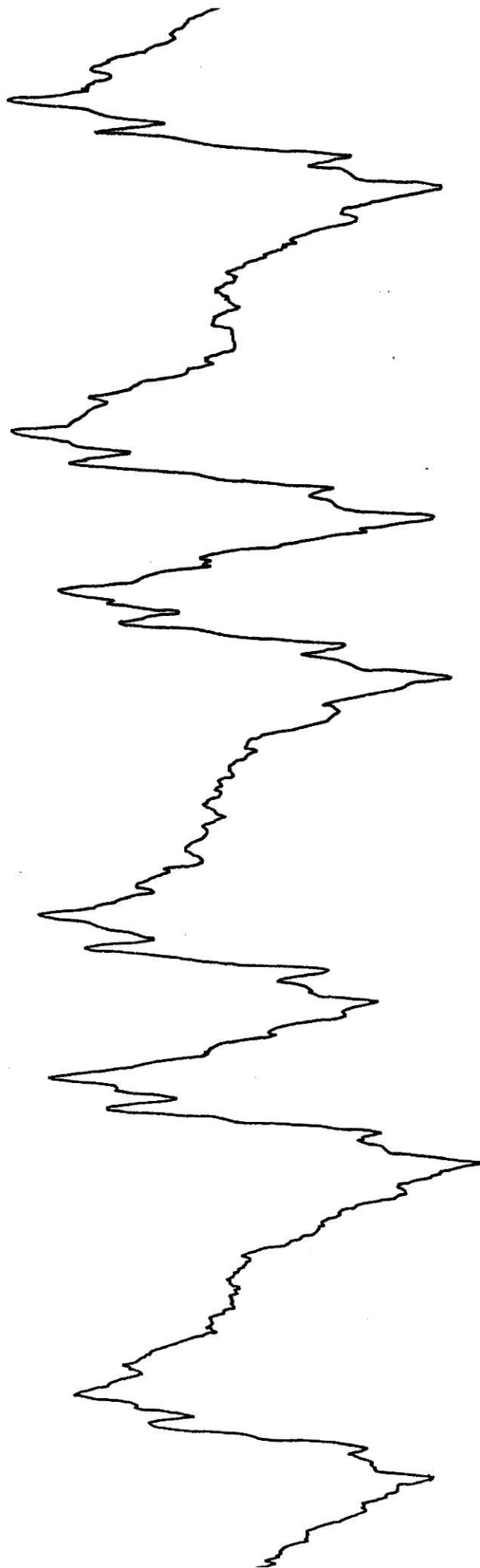


Figure 15. Electron spin resonance spectrum of the N-iso-propylmethanesulfonamido radical.



10 GAUSS

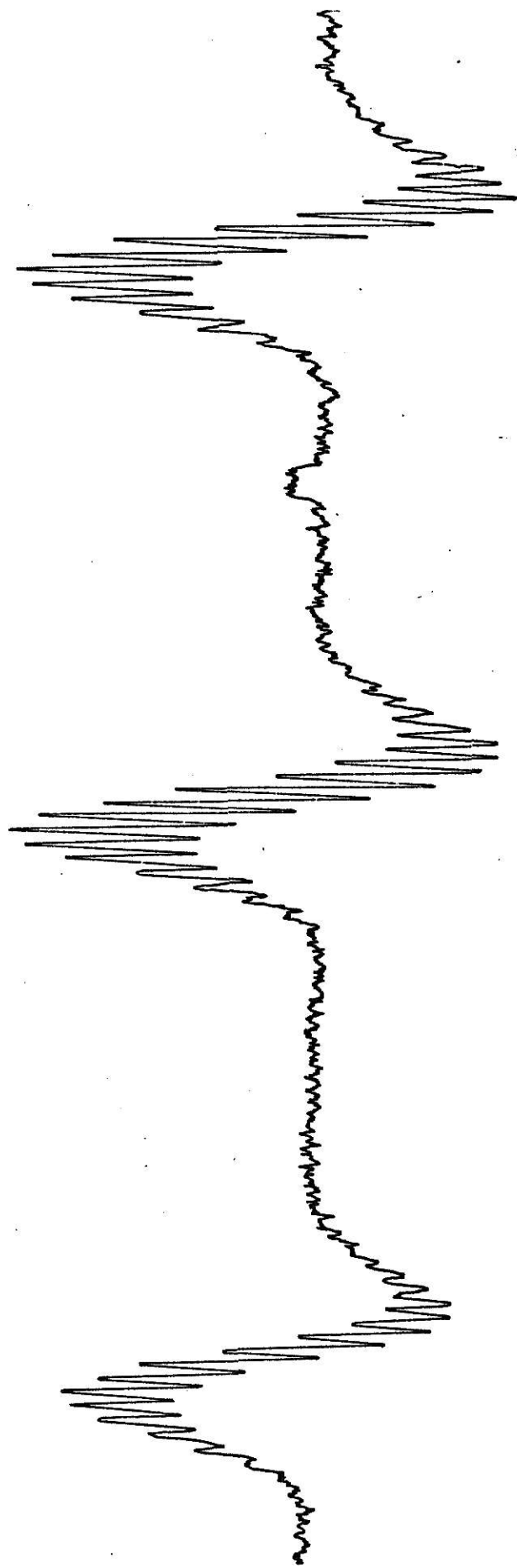


Figure 16. Electron spin resonance spectrum of the N-tert-butylmethanesulfonamido radical.

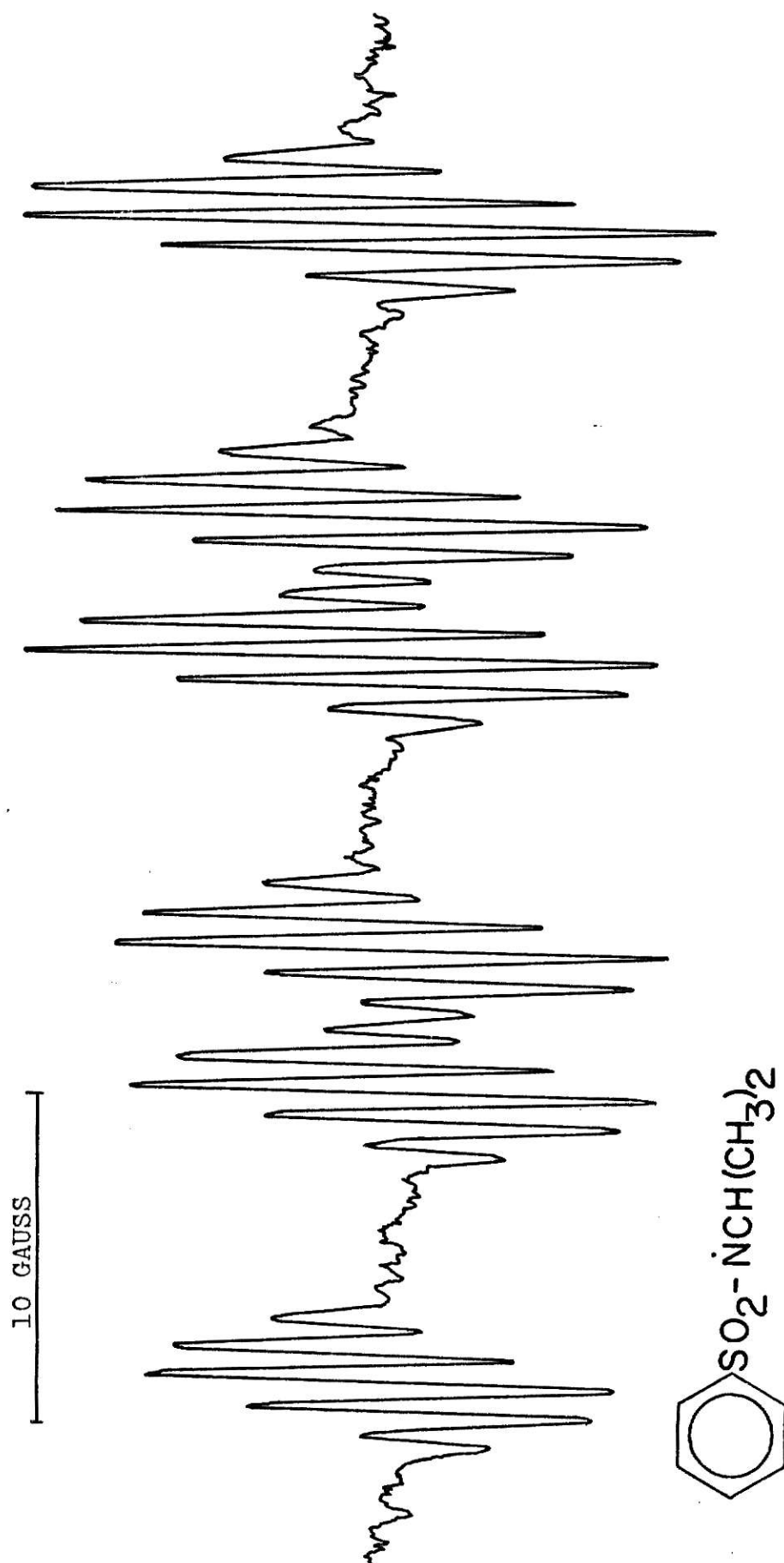


Figure 17. Electron spin resonance spectrum of the N-iso-propylphenylsulfonamido radical.

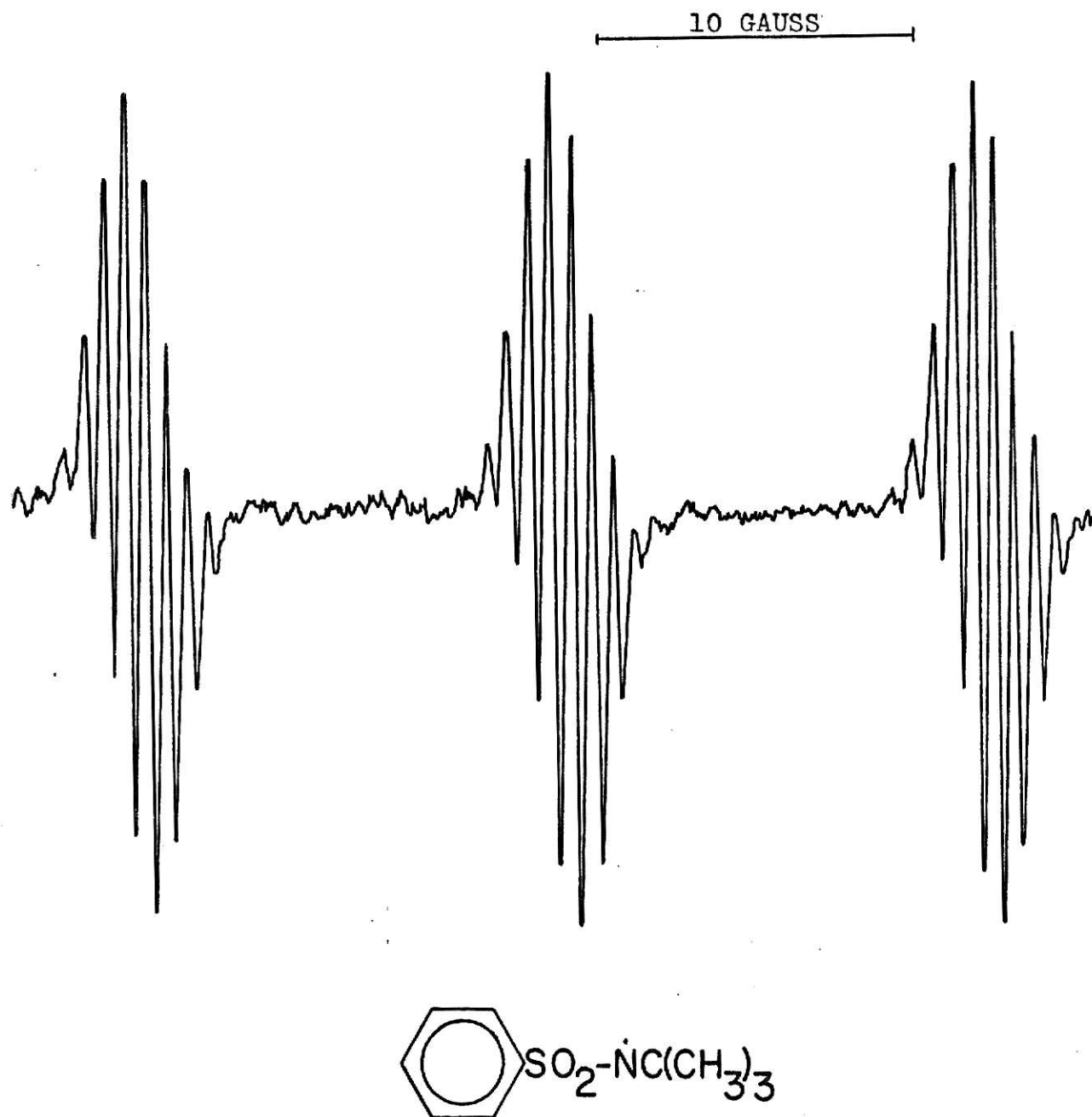


Figure 18. Electron spin resonance spectrum of the N-tert-butylphenylsulfonamido radical.

Table IX

Spectral Parameters<sup>a</sup> of Simple Sulfonamido Radicals<sup>b</sup>

<u>R-SO<sub>2</sub>-N-R'</u>		<u>N</u> <u>a</u>	<u>H</u> <u>a<sub>B</sub></u> <u>c</u>	<u>H</u> <u>a<sub>γ</sub></u> <u>c</u>	<u>H</u> <u>aSO<sub>2</sub>CH<sub>3</sub></u> <u>c</u>	<u>g</u> <u>value</u> <u>d</u>	<u>Temp., °C</u>
<u>R</u>	<u>R'</u>						
CH <sub>3</sub>	CH <sub>3</sub>	13.4 <sup>c</sup>	29.7 <sup>c</sup>			2.0041	30
CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	13.2 <sup>c</sup>	35.7 <sup>c</sup>			2.0041	30
CH <sub>3</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	13.09	8.70	0.92 <sup>c</sup>		2.0041	0
CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	13.32		0.33	1.03	2.0041	-20
C <sub>6</sub> H <sub>5</sub>	CH(CH <sub>3</sub> ) <sub>2</sub>	13.07	8.82	0.98		2.0042	0
C <sub>6</sub> H <sub>5</sub>	C(CH <sub>3</sub> ) <sub>3</sub>	13.30		0.64		2.0042	0

a Reported in gauss, estimated accuracy  $\pm 0.7\%$ , except where noted

b Cyclopropane used as the solvent

c Estimated accuracy  $\pm 2\%$  due to poor signal to noise ratio

d Corrected to second order, estimated accuracy  $\pm 0.0001$

Differences could be noted for the  $\gamma$ -hydrogen hfsc's which were not resolved in the case of the amido radicals but were seen in the spectra of N-iso-propyl and N-tert-butyl substituted sulfonamido radicals (see following Figures 15 through 18). Changing R from methyl to phenyl while keeping R' constant did not change the overall coupling pattern (compare Figure 15 with 17 and Figure 16 with 18). The spectra were dominated by the 1:1:1 triplet due to the nitrogen nucleus, split into a smaller 1:1 doublet if an iso-propyl group was adjacent to this atom (Figure 15 and 17). Additional splittings of the order of 1 gauss or less were assigned to  $\gamma$ -protons and/or the methanesulfonyl hydrogen atoms,  $\text{CH}_3\text{-SO}_2\text{-}$ , with better resolution of  $\gamma$ -splittings in case of the phenylsulfonamides. Table IX summarizes the spectral parameters for the observed sulfonamido radicals.

The nitrogen hyperfine splitting constants of ca. 13 G and g values of 2.0041 and 2.0042 suggested a II electronic configuration as the values were consistent with other nitrogen-centered II radicals reported in the literature<sup>18,27,31,36,42</sup> and similar to the parameters measured for amido radicals. The magnitude of the N-methyl proton hfsc furthermore indicated that there was no extensive delocalization of spin density into the sulfonyl group, a result that was also derived for amido radicals on the basis of experimental data. This indicated that the sulfonyl and the carbonyl group exhibited very similar electronic effects on adjacent atoms bearing an unpaired electron.

Likewise, the dependence of the  $\beta$ -hydrogen hfsc's on the alkyl substitution was found to be similar to that derived for dialkyl-amino<sup>31</sup> and N-alkylpivalamido radicals (Table X).

Table X  
Spectral Parameters<sup>a</sup> for  $\beta$ -Hydrogens in  
Related Nitrogen-Centered II Radicals

Substituent Group R	Radical $\beta$ -Hfsc's		
	$\text{R}_2\text{N}^{\cdot\text{b}}$	$(\text{CH}_3)_3\text{CC}(\text{O})\text{NR}^{\cdot\text{c}}$	$\text{CH}_3\text{SO}_2\text{NR}^{\cdot\text{d}}$
$\text{CH}_3$	27.36	29.30	29.7
$\text{C}_2\text{H}_5$	36.90	37.8	35.7
$\text{CH}(\text{CH}_3)_2$	14.31	22.10	8.70 <sup>e</sup>

<sup>a</sup> Hfsc's reported in gauss

<sup>b</sup> Reference 31, spectra obtained at  $-90^\circ$

<sup>c</sup> This work, spectra obtained at  $-100^\circ$

<sup>d</sup> This work, spectra obtained at  $30^\circ$ , except where noted

<sup>e</sup> Hfsc measured at  $0^\circ$

On the basis of the foregoing discussion in Part I this dependence, a larger hfsc for the N-ethyl substituted sulfonamido radical and a smaller one for the N-iso-propyl derivative compared with the value of the N-methylsulfonamido radical, indicated a restricted rotation about the N-C bond which was suggestive of a bent S-N-C geometry. From previous considerations it seemed likely that the corresponding angle at the radical center would be of the order of  $120^\circ$ .

Application of the INDO method to these radicals containing a second row element was not attempted since a parameterization which did not include 3d orbitals in the basis set had only

been found adequate in calculations involving Si and Cl.<sup>79</sup>

Temperature dependence studies of the  $\beta$ -hydrogen hfsc's for the N-iso-propylphenylsulfonamido radical gave further evidence for a hindered rotation. A large effect was noted for this specific coupling constant of this radical which indicated an energy barrier to rotation about the N-C bond.

Table XI

$\beta$ -Hydrogen Hfsc's vs. Temperature for the  
N-iso-Propylphenylsulfonamido Radical

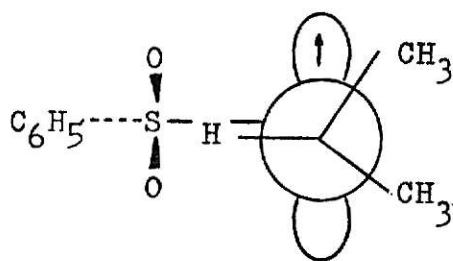
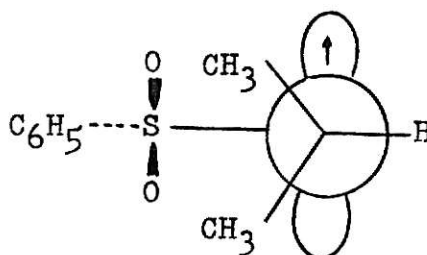
$\text{C}_6\text{H}_5\text{-SO}_2\text{-}\dot{\text{N}}\text{-CH(CH}_3)_2$ $\beta\text{-Hfsc}^{\text{a}}$	Temperature, $^{\circ}\text{C}^{\text{b}}$
7.36	-80
7.36	-60
8.00	-40
8.51	-20
8.82	0
9.43	20
10.01	40
10.91	60

<sup>a</sup> Spectra obtained in cyclopropane, hfsc's reported in gauss, estimated accuracy  $\pm 0.7\%$   
<sup>b</sup> Estimated accuracy  $\pm 3^{\circ}$

From Table XI it could be seen that the  $\beta$ -hydrogen hfsc increased as the temperature increased, changing about 3.5 G over the temperature

range from  $-80^{\circ}$  to  $+60^{\circ}$ . Assuming an electronic configuration in which the unpaired electron resided in a 2p orbital on nitrogen perpendicular to the S-N-C plane it could be inferred from the observed temperature effect that at lower temperatures the methine hydrogen of the iso-propyl group preferred an alignment in the nodal plane of this orbital, accounting for the small hfsc's. With increasing temperatures this C-H bond slowly approached, on the time-average, an eclipsed conformation with the spin bearing orbital. At higher temperatures this hfsc theoretically should reach the value observed for the N-methyl protons which, however, could not be shown experimentally due to the insufficient steady-state concentration of this radical at higher temperatures.

In order to be able to obtain the energy barrier to rotation by the method described by Krusic and Kochi<sup>67</sup> a simple twofold sinusoidal potential for this rotation would be required. Such a potential most likely did not exist for the N-iso-propylphenylsulfonamido radical as rotation about the N-C bond would eclipse the methyl groups of the iso-propyl moiety and the oxygen atoms of the sulfonyl group. Therefore the energy corresponding to structure 31 should be higher than the energy corresponding to conformer 30.

3031

## 2. Evidence for a Cyclic Sulfonamido Radical

The spectral similarities to the carboxyamido radicals but an enhanced stability at higher temperatures led to the conclusion to attempt spectra of cyclic sulfonamido radicals. Thus N-chloropropanesultam was synthesized as shown in the reaction sequence in Figure 19, following the synthetic route given by Bliss and his co-workers.<sup>77</sup>

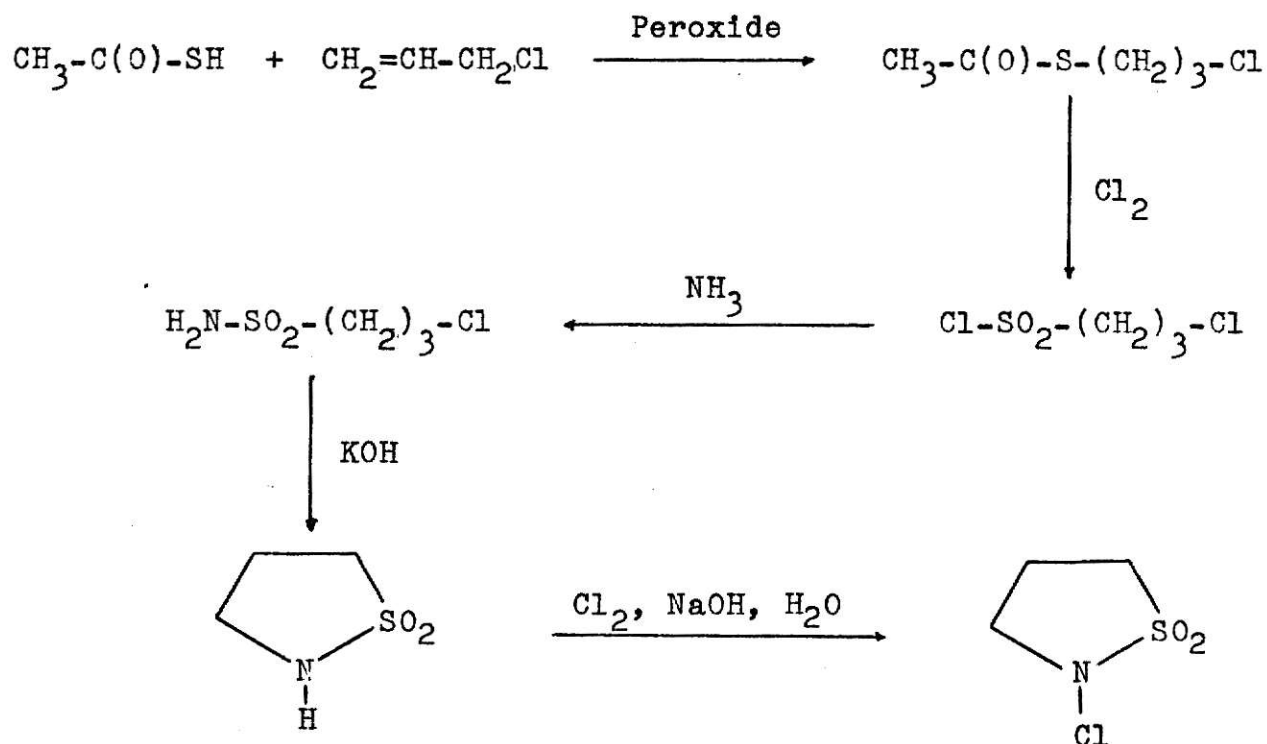


Figure 19. Synthesis of N-chloropropanesultam

Photolyzing this compound at 30° in cyclopropane very weak esr signals were detected (Figure 20). Unfortunately not the complete spectrum could be recorded due to the instability of this ra-

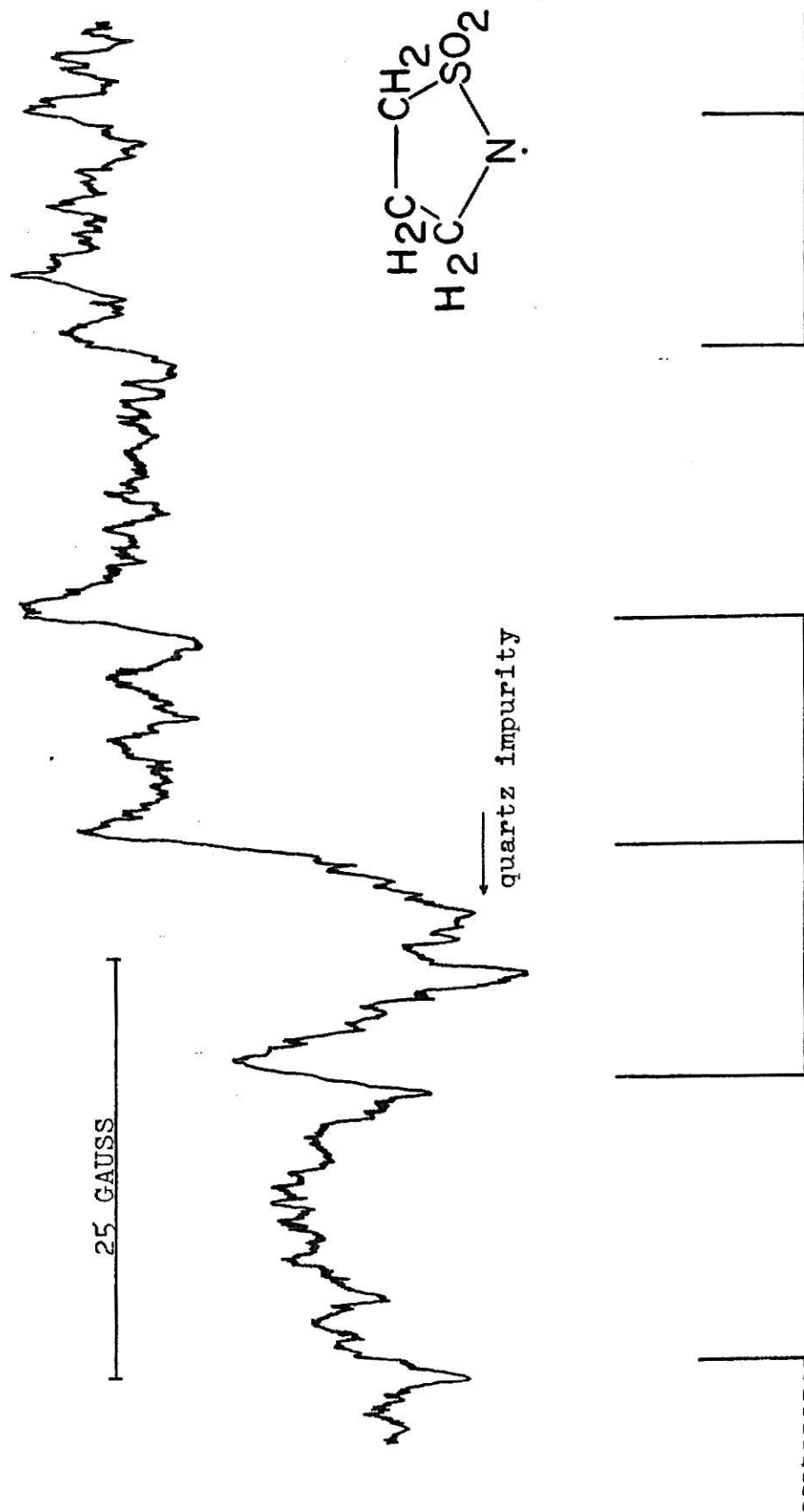
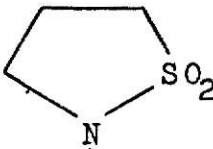


Figure 20. Partial electron spin resonance spectrum of the nitrogen-centered radical derived from N-chloro-propanesultam.

dical. By comparison with the acyclic N-ethylmethanesulfonamido radical in which a methylene group was likewise adjacent to the nitrogen radical center an assignment of the lines which were present in the expected intensity ratios as indicated by the stick diagram was possible (summary of spectral parameters in Table XII).

Table XII

Spectral Parameters<sup>a</sup> of a Cyclic and an Acyclic Sulfonamido Radical<sup>b</sup>

Radical	$a_N$	$a_\beta^H$	$g$ value <sup>d</sup>	Temp., °C
	13.3 <sup>c</sup>	43.4 <sup>c</sup>	2.0042	30
$\text{CH}_3\text{-SO}_2\text{-}\dot{\text{N}}\text{-C}_2\text{H}_5$	13.2	35.7	2.0041	30

<sup>a</sup> Hfsc's reported in gauss, estimated accuracy  $\pm 2\%$  except where noted

<sup>b</sup> In cyclopropane as the solvent

<sup>c</sup> Estimated accuracy  $\pm 5\%$  due to poor signal to noise ratio

<sup>d</sup> Corrected for second order effects, estimated accuracy  $\pm 0.0001$

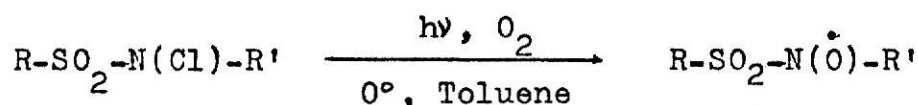
The nitrogen hfsc and the  $g$  value were consistent with the other sulfonamido radical whereas the splitting constant for the  $\beta$ -protons was ca. 8 G larger than in the acyclic N-ethyl substituted radical. But this increase was expected since the more rigid ring structure would align the two  $\beta$ -hydrogen atoms closer (by approximately  $5^\circ$ )

with the spin bearing 2p orbital on nitrogen. On the other hand, it was not possible to obtain any spectrum by x-irradiating N-chloropropanesultam in an adamantane matrix at low temperatures although one would expect a spectrum similar to the one obtained from N-chloro-ε-caprolactam (Figure 12) with this technique. A reason for this discrepancy remained speculative. But the spectrum recorded in solution gave some direct evidence for the fact that an initial formation of a nitrogen-centered radical, with the same electronic configuration as the open chain counterparts, occurred upon photolysis of the N-chloro compound. Once formed, several modes for elimination and rearrangement reactions might have been possible that would not seem likely for acyclic radicals, explaining the very transient nature of the cyclic species. Due to the five membered ring the substituent groups on the nitrogen radical center were tied back and held in close proximity with an S-N-C angle of probably ca. 120°. A similar geometry could be expected for the acyclic sulfonamido radicals on the basis of the congruent esr parameters. This would support their II electronic configuration in terms of the discussion of INDO calculations given earlier since sulfonamido and amido radicals seemed to be very much alike in electronic ground state configurations.

### 3. Generation and Identification of Sulfonyl Nitroxides

By photolyzing N-chloroamides in toluene in the presence of oxygen, spectra of the corresponding acyl nitroxides were obtained. Extrapolating these results it seemed likely that spectra of sulfonyl

nitroxides,  $R-SO_2-N(\dot{O})-R'$ , should be obtained in a similar fashion. Thus two N-chlorophenylsulfonamides were photolyzed in air-saturated toluene (ca. 10% by volume) at  $0^\circ$  in the previously described manner. Exposure to the uv light source for ca. 10 sec. produced esr spectra which were assigned to the corresponding sulfonyl nitroxides.



The spectrum assigned to the N-iso-propylphenylsulfonyl nitroxide (Figure 21) featured a characteristic 1:1:1 nitrogen triplet and a relatively small 1:1 doublet assigned to the methine proton. The identity of these radicals was unequivocally established by their

Table XIII

Spectral Parameters<sup>a</sup> of Sulfonyl Nitroxides

Radical	$a_N$	$a_{H\gamma}$	g value	Reference
$C_6H_5-SO_2-N(\dot{O})-CH(CH_3)_2$	11.44	1.99	2.0062	This work <sup>b</sup>
"	11.5	2.3	2.0061	80 <sup>c</sup>
$C_6H_5-SO_2-N(\dot{O})-C(CH_3)_3$	12.17		2.0059	This work <sup>b</sup>
"	12.2		2.0061	80 <sup>c</sup>

<sup>a</sup> Hfsc's reported in gauss

<sup>b</sup> Estimated accuracy of hfsc's  $\pm 0.7\%$ , spectra obtained in toluene at  $0^\circ$

<sup>c</sup> Spectra obtained in toluene or methylene chloride at room temperature

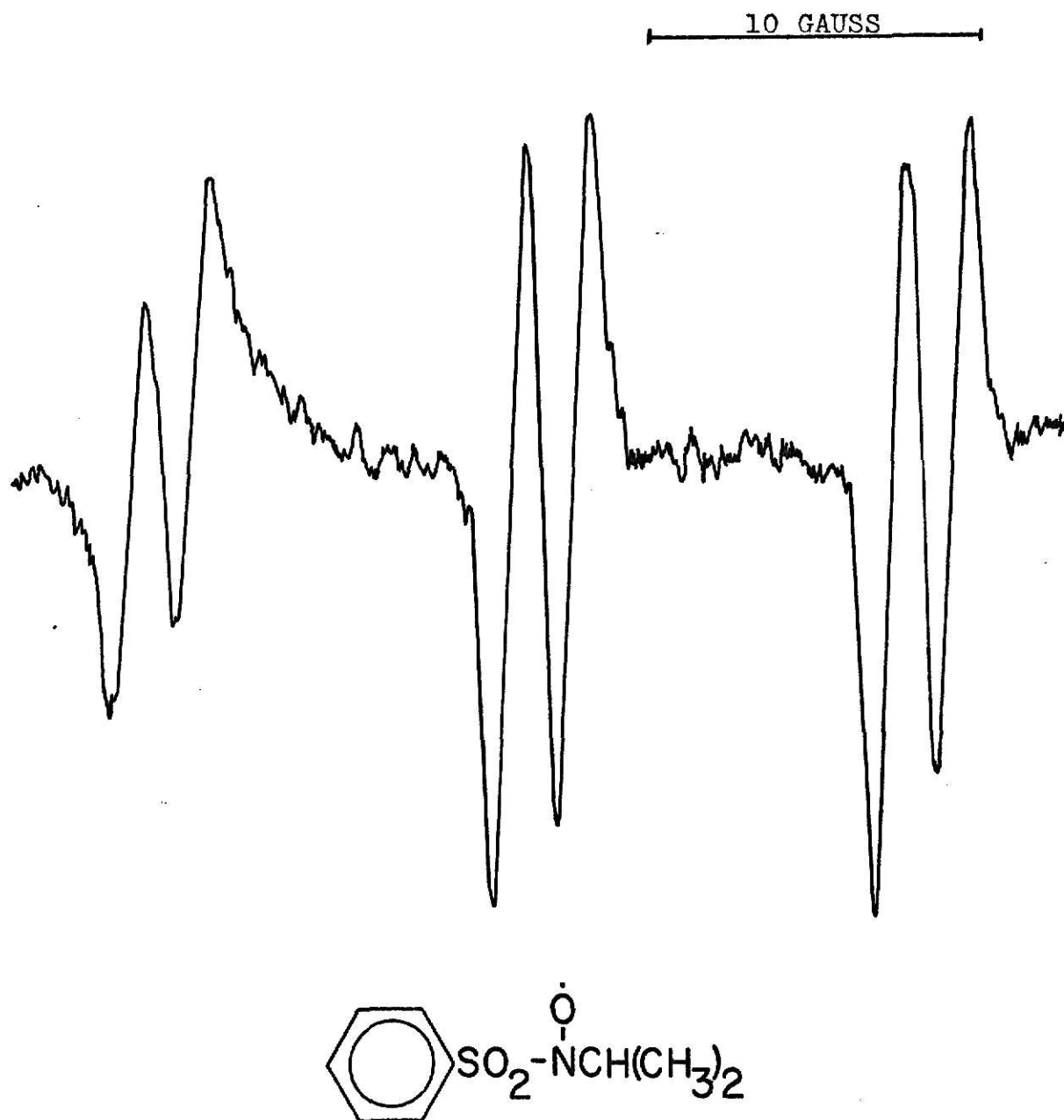


Figure 21. Electron spin resonance spectrum assigned to the N-iso-propylsulfonyl nitroxide.

mode of generation, their characteristic  $g$  values which agreed with the values obtained for acyl nitroxides, and comparison with reported sulfonyl nitroxides. DeBoer and his coworkers<sup>80</sup> had obtained sulfonyl nitroxides upon lead dioxide treatment of N-hydroxylsulfonamides and upon photolysis of N-nitrososulfonamides. The spectral parameters were compared in Table XIII.

A similar trapping mechanism as had been assumed for the formation of acyl nitroxides could also be applied in this case suggesting the initial photolytic generation of a sulfonamido radical and subsequent reaction with oxygen present in the system, leading to the formation of nitroxides.

### III. EXPERIMENTAL

#### A. The Esr Experiment

##### 1. Esr Spectrometer

The electron spin resonance (esr) spectra were recorded on a Varian Model 4502 X-Band spectrometer. The standard Varian variable temperature dewar was used when spectra were recorded at temperatures other than room temperature. The spectra were obtained with experimental samples in the front cavity modulated at 100 kHz and an aqueous Fremy's salt solution in the rear cavity modulated at 200 or 400 Hz. Spectra of both the experimental sample and Fremy's salt were recorded simultaneously on a G-22 dual channel recorder.

Hyperfine coupling constants (hfsc's) and g values of the radicals were derived by comparison with the hfsc and g value of Fremy's salt which were taken to be 13.09 G and 2.0055, respectively.<sup>81</sup> The calculation of g values was performed as described by Kensler.<sup>82</sup>

Those spectra the hfsc's of which could not be obtained directly due to overlapping lines were derived from computer simulations, using a program which included second order effects<sup>39</sup> obtained from P. J. Krusic at E. I. DuPont de Nemours Company.<sup>38</sup>

##### 2. Photolytic Apparatus

A PEK AH6-2B, 2000 W high pressure mercury capillary lamp was utilized in conjunction with a suitable lens system as described by Kensler<sup>82</sup> with modifications and operational considerations added by

West.<sup>41</sup> In general, as many samples as could conveniently be prepared were made ready for photolysis. Samples were changed in the esr cavity without turning the lamp off in order to reduce the times the lamp had to be started since the lamp lifetime was reduced each time the lamp was started. Since the lamp was operated in a vertical position readjustment of the mercury in the capillary of the lamp had to be made after four to six hours of lamp operation.

### 3. Sample Preparation and Generation of Radicals

#### a. Amido and Sulfonamido Radicals

Amido and sulfonamido radicals were generated by photolysis of the corresponding N-chloroamides and -sulfonamides, respectively, directly in the cavity of the esr spectrometer. The esr samples were generally prepared in the same manner using high vacuum techniques to deoxygenate the samples. As the N-chloro compounds were non-volatile substances the proper amount was transferred into the esr sample tubes by a long pipette. The amides were deoxygenated by at least three freeze-pump-thaw cycles. The cyclopropane (Matheson Company) used as a solvent was deoxygenated on the vacuum system by usually two freeze-pump-thaw cycles, then trap to trap distilled into the esr sample tube containing the N-chloro compound. Samples were approximately 10-20% by volume of the amide in cyclopropane. The sample tubes were then sealed and stored at  $-196^{\circ}$  until used. The solutions in the esr tubes were warmed to  $-80^{\circ}$  and thoroughly mixed before placing in the esr variable temperature dewar cavity prior to photolysis.

The vacuum system employed maintained a vacuum of less than  $10^{-5}$  Torr. The sample tubes used were described by Kensler.<sup>34</sup> Photolyses were carried out with samples in the esr cavity using the focused 2000 W high pressure mercury lamp.

b. Acyl and Sulfonyl Nitroxides

Spectra of acyl and sulfonyl nitroxides were observed upon photolysis of N-chloroamides and -sulfonamides, respectively, in air-saturated toluene at reduced temperatures. Samples were simply prepared by mixing toluene and the N-chloro compound (ca. 10% by volume) without deoxygenation. The nitroxides were produced by brief exposure (ca. 10 sec) to the light source using a 25% transmittance screen in front of the uv lamp. Spectra of acyl nitroxides were recorded at  $-90^{\circ}$  whereas of sulfonyl nitroxides were obtained at  $0^{\circ}$  due to an enhanced stability. The esr spectra remained for several minutes after removing the light source with a gradually decreasing intensity but upon repeated exposure to the light source the initial intensity was regained.

c. Radicals Generated in an Adamantane Matrix

Radicals from N-chloro-N-tert-butylformamide and N-chlorolactams were generated by x-irradiation in an adamantane matrix (Aldrich Chemicals) utilizing the procedure of Wood and Lloyd.<sup>46-48</sup> As the N-chloro compounds were non-volatile substances cyclohexane was used as a cosolvent. After evaporation the solvent some of the amide was trapped in the adamantane matrix. The dried substance was transferred into an esr sample tube and x-irradiated with a Norelco x-ray

diffraction unit. A copper target was used and operated at 45 kV and 20 mA. The sample was placed about two inches away from the target and x-irradiated for two hours at  $-196^{\circ}$ . Isotropic spectra were generally recorded after allowing the sample to warm up to room temperature in the cavity of the esr spectrometer.

## B. INDO Calculations

The INDO calculations were performed on an IBM 360/50 computer utilizing the program of Pople, et al.<sup>52,53</sup> A copy of this program was obtained from the Quantum Chemistry Program Exchange, Indiana University, No. 141. The standard program was modified by Purcell<sup>59</sup> to allow calculations on amido radicals in the  $\Pi$  electronic configuration. The Cartesian coordinates for all the atoms in a molecule were calculated using a program described by Schwendeman.<sup>83</sup> A geometry for a given molecule was assumed using bond lengths (in ångström units) and bond angles as standardized in Pople's model "A".<sup>53</sup> Energy-minimization with respect to the geometry was accomplished by variation of one parameter (first bond lengths then angles) until optimization with respect to this parameter was achieved while keeping the remaining part of the molecule constant. The bond lengths were optimized to 0.01 Å, bond angles to  $1^{\circ}$ . The hfsc for a freely rotating methyl group was approximated by averaging the calculated hyperfine interactions of three methyl rotamers.

### C. Chemicals

Melting points were obtained on a calibrated Fisher-Johns melting point apparatus. Boiling points were recorded while distilling the materials and were uncorrected. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian T-60 spectrometer and chemical shifts were reported relative to tetramethylsilane (TMS). The infrared (ir) spectra were recorded on a Perkin-Elmer Model 137 spectrometer and calibrated with the 6.23  $\mu$  line of polystyrene film.

#### 1. N-Chloroamides

The N-chloro-N-alkylamides were obtained by treatment of the corresponding amides with tert-butylhypochlorite in the presence of small amounts of potassium carbonate in an inert solvent, usually carbon tetrachloride, at room temperature for several hours as described by Neale, et al.<sup>5</sup> Completion of the chlorination was determined by the disappearance of the N-H stretching band (ca. 3.0  $\mu$ ) in the ir spectrum and the disappearance of the broad absorption peak due to the amide proton in the nmr spectrum. Additionally, a characteristic downfield shift of up to 0.8 ppm of the  $\beta$ -protons adjacent to the N-Cl bond was noted when comparing nmr spectra with the parent amides. A direct identification of the N-Cl bond formation by spectroscopic methods did not seem suitable since the N-Cl stretching band was in the fingerprint region of the ir spectrum (12.5  $\mu$  to 13.2  $\mu$ )<sup>84</sup> where an unambiguous assignment did not seem possible. Likewise, identification by uv/visible spectroscopy was not useful

as the carbonyl group adjacent to the nitrogen atom of the N-Cl chromophore removed the selective absorption of the N-Cl bond.<sup>85</sup>

The tert-butylhypochlorite used in these syntheses was initially prepared by the method of Teeter and Bell<sup>86</sup> in 50 to 70% yield by passing chlorine into an aqueous sodium hydroxide solution in the presence of tert-butyl alcohol at 5-10° for two hours. Although a higher yield was obtained in this manner a second method described by Mintz and Walling<sup>87</sup> proved more convenient in avoiding the use of gaseous chlorine. A mixture of tert-butyl alcohol and glacial acetic acid was added dropwise to a common household bleach solution at ice bath temperatures and stirred for several minutes. The tert-butylhypochlorite which separated as the upper layer was washed acid free and stored over 4 Å molecular sieves in the dark in the refrigerator with no noticeable loss in activity after several weeks.

N-Chloro-N-methylacetamide. The synthesis of N-chloro-N-methylacetamide was achieved in 58% yield from 4.25 g (0.058 mol) N-methylacetamide (commercially available) and 7.0 g (0.065 mol) tert-butylhypochlorite according to the procedure of Neale, et al.:<sup>5</sup> bp 45-47°, 15 mm (lit.<sup>88</sup> 52°, 50 mm).

N-Chloro-N-tert-butylacetamide. The N-tert-butylacetamide used in this preparation was synthesized in 74% yield from acetyl chloride and tert-butylamine according to the method of Treibs, et al.:<sup>89</sup> mp 100-101° (lit.<sup>90</sup> 97-98°). The synthesis of the N-chloro compound was achieved in 42% yield from 6.7 g (0.058 mol) amide and 7.0 g (0.065 mol) tert-butylhypochlorite following the method of Neale, et al.:<sup>5</sup> bp 65-67°, 15 mm (lit.<sup>5</sup> 44°, 9 mm).

N-Chloro-N-methylpivalamide. The synthesis of the parent amide was achieved in 79% yield by the dropwise addition of 12.0 g (0.10 mol) pivaloyl chloride to a solution of 8.0 g (0.025 mol) monomethylamine (bp  $-6^{\circ}$ ) in 100 ml ether at ice bath temperatures: mp  $88-90^{\circ}$  of the crude product. Reaction of 4.5 g (0.039 mol) N-methylpivalamide with 4.7 g (0.043 mol) tert-butylhypochlorite in the previously described manner afforded the N-chloro-N-methylpivalamide in 54% yield: bp  $67-71^{\circ}$ , 15 mm (lit.<sup>88</sup>  $65^{\circ}$ , 25 mm).

N-Chloro-N-tert-butylformamide. To 9.0 g (0.089 mol) tert-butylformamide (commercially available) was added 10.0 g (0.092 mol) tert-butylhypochlorite according to the method of Neale, et al.,<sup>5</sup> to give the N-chloro compound in 37% yield: bp  $48-49^{\circ}$ , 1.5 mm (lit.<sup>91</sup>  $48-52^{\circ}$ , 0.1-0.15 mm; the reported pressure might be a printing error).

N-Chloro-N-ethylpivalamide. The N-ethylpivalamide used in this preparation was synthesized in 82% yield from 12.0 g (0.010 mol) pivaloyl chloride and 17.2 g (0.25 mol) monoethylamine (bp  $16^{\circ}$ ) in the same manner as N-methylpivalamide. Treatment of 7.0 g (0.054 mol) of the crude amide with 6.5 g (0.060 mol) tert-butylhypochlorite in 75 ml carbon tetrachloride in the presence of 0.1 g potassium carbonate for 48 hours gave the N-chloro-N-ethylpivalamide in 34% yield: bp  $28-29^{\circ}$ , 1 mm; ir ( $\text{CCl}_4$ )  $6.02 \mu$  ( $\text{C}=\text{O}$ ); nmr ( $\text{CDCl}_3$ )  $\tau$  8.77 and 8.66 (3 + 9 H, triplet and singlet, overlapping methyl and tert-butyl group,  $J = 7.0$  Hz), 6.26 (2 H, quartet,  $J = 7.0$  Hz). See page 88 for ir and nmr spectra.

N-Chloro-N-iso-propylpivalamide. Preparation of the crude parent amide (mp  $93-95^{\circ}$ ) was achieved in 62% yield from 12.0 g (0.10 mol)

pivaloyl chloride and 15.0 g (0.25 mol) iso-propylamine in a similar manner as had been described for N-methylpivalamide. The synthesis of the N-chloroamide was achieved in 39% yield from 6.0 g (0.042 mol) N-iso-propylpivalamide and 5.4 g (0.050 mol) tert-butylhypochlorite utilizing the method of Neale, et al.:<sup>5</sup> bp 38-40°, 1 mm; ir (CCl<sub>4</sub>) 6.03  $\mu$  (C=O); nmr (CDCl<sub>3</sub>)  $\tau$  8.82 (6 H, doublet,  $J$  = 6.6 Hz), 8.65 (9 H, singlet), 5.13 (1 H, septet,  $J$  = 6.6 Hz). See page 90 for ir and nmr spectra.

N-Chloro- $\epsilon$ -caprolactam. The synthesis of N-chloro- $\epsilon$ -caprolactam was achieved in 37% yield from 2.5 g (0.022 mol)  $\epsilon$ -caprolactam (commercial reagent) and 2.7 g (0.025 mol) tert-butylhypochlorite in the previously described manner. A colorless liquid was obtained. No distillation was attempted since this N-chloro compound was known to decompose at 80°, 760 mm.<sup>92</sup>

N-Chloro-2-pyrrolidinone. 5.1 g (0.060 mol) 2-pyrrolidinone (commercial reagent) were treated with 7.0 g (0.065 mol) tert-butylhypochlorite following the procedure of Neale, et al.,<sup>5</sup> to give the N-chloro compound in 77% yield. The colorless crystals obtained melted at 42-44°, the ir showed no N-H stretching band.

N-Chloro-5,5-dimethyl-2-pyrrolidinone. The synthetic route given by Moffett<sup>71,93</sup> was followed in the preparation of 5,5-dimethyl-2-pyrrolidinone. In a 500 ml three-necked flask, fitted with a stirrer, a dropping funnel, and a thermometer, 89.0 g (1.0 mol) redistilled 2-nitropropane (bp 120°), 50 ml dioxane, and 10 ml of a 40% methanolic solution of benzyltrimethylammonium hydroxide (Triton B) were warmed to 70°. 86.0 g (1.0 mol) redistilled methyl acrylate (bp 80°)

were added with stirring during 15 min. The temperature rose to about 100° during the addition and then dropped to about 85°. The mixture was heated with stirring on a steam bath for four hours. After cooling and acidification with dilute hydrochloric acid the product was extracted with four 50 ml portions of ether. The ether layer was washed with water, 0.1% sodium bicarbonate solution, and finally again with water. The ethereal solution was dried over anhydrous sodium sulfate. After filtration and removal of the solvent by distillation the product was distilled through a short fractionating column. The methyl  $\gamma$ -methyl- $\gamma$ -nitrovalerate was obtained in 74% yield: bp 129°, 1.5 mm (lit.<sup>93</sup> 79°, 1 mm).

A different catalyst than described by Moffett<sup>93</sup> was used for the reduction of the nitro compound. To a solution of 15.0 g (0.086 mol) methyl  $\gamma$ -methyl- $\gamma$ -nitrovalerate in 200 ml absolute ethanol 1.5 g of palladium on powdered charcoal (5%) were added. The mixture was hydrogenated at room temperature for 45 hours starting with an initial pressure of 60 psi. The catalyst was filtered and the ethanol removed by distillation. The residue was heated to 200° and kept at this temperature for 10 min. After cooling the product was distilled through a short distillation apparatus: bp 148-152°, 15 mm (lit.<sup>93</sup> 126.5-128.5°, 12 mm). The 5,5-dimethyl-2-pyrrolidinone was obtained in only 26% yield, probably due to the catalyst employed.

The synthesis of N-chloro-5,5-dimethyl-2-pyrrolidinone was achieved in 42% yield from 2.5 g (0.021 mol) 5,5-dimethyl-2-pyrrolidinone and 2.7 g (0.025 mol) tert-butylhypochlorite following the synthetic method given by Neale, et al.:<sup>5</sup> bp 75-78°, 1.5 mm; ir (CCl<sub>4</sub>)

5.79  $\mu$  (C=O); nmr ( $\text{CCl}_4$ )  $\tau$  8.72 (6 H, singlet), 7.8 (4 H, multiplet).

See page 92 for ir and nmr spectra.

N-Chloro-3,5,5-trimethyl-2-pyrrolidinone. The synthesis of 3,5,5-trimethyl-2-pyrrolidinone was achieved in 57% yield following the procedure given for 5,5-dimethyl-2-pyrrolidinone, except redistilled methyl methacrylate (bp 99-100°) was used as a starting material. The N-chloro compound was synthesized in 52% yield from 4.0 g (0.032 mol) 3,5,5-trimethyl-2-pyrrolidinone and 4.0 g (0.037 mol) tert-butylhypochlorite in the previously described manner.<sup>5</sup> A white crystalline solid was obtained: mp 75°; ir and nmr spectra showed no presence of the amide proton.

N-Chloro- $\beta$ -iso-valerolactam. The starting  $\beta$ -iso-valerolactam-N-sulfonyl chloride was synthesized according to the method described by Graf.<sup>94</sup> A 300 ml four-necked flask was fitted with a mechanical stirrer, a dry ice-jacketed dropping funnel, a thermometer, and a dry ice reflux condenser. The flask was cooled down to -20° by means of a dry ice-acetone bath while 67 ml of sulfur dioxide were condensed into the flask. 47.1 g (0.33 mol) chlorosulfonyl isocyanate (commercially available) and 0.3 g potassium chloride were added. 19.5 g (0.35 mol) iso-butylene, previously condensed in a cold trap, were added to the dropping funnel. The temperature in the reaction flask was lowered to -60° and the iso-butylene was added dropwise to the stirred solution during 20 min. The cooling bath was removed and the reaction mixture allowed to warm until the sulfur dioxide started refluxing. The slightly yellow liquid obtained was added gradually to 125 ml water with vigorous stirring. A white preci-

pitrate formed and sulfur dioxide evolved. Dissolved sulfur dioxide was removed by means of an air stream directed on the surface of the liquid. The precipitate was collected on a Buchner funnel and washed three times with 30 ml portions of ice water. The moist product obtained in this manner was converted directly to the  $\beta$ -iso-valerolactam utilizing the method of Durst and O'Sullivan.<sup>95</sup>

A solution of 35.6 g of the crude  $\beta$ -iso-valerolactam-N-sulfonyl chloride dissolved in 200 ml ether was added dropwise to a mixture of 25% (by weight) aqueous sodium sulfite solution and 50 ml ether at room temperature. At the same time a 10% (by weight) aqueous potassium hydroxide solution was added to maintain the pH of the reaction mixture at 8. After completion of the addition the ether layer was separated and dried over anhydrous sodium sulfate, then the ether was removed by distillation. The lactam, distilled at reduced pressure: bp 75-83°, 1.5-1.75 mm (lit.<sup>94</sup> 70°, 1 mm), was obtained in 26% yield based on chlorosulfonyl isocyanate.

Conversion to the N-chloro- $\beta$ -iso-valerolactam was achieved in 31% yield by the reaction of 2.0 g (0.020 mol)  $\beta$ -iso-valerolactam with 2.7 g (0.025 mol) tert-butylhypochlorite as previously described: bp 50-52°, 1 mm; ir (neat) 5.6  $\mu$  (C=O); nmr (CDCl<sub>3</sub>)  $\tau$  8.55 (6 H, singlet), 7.09 (2 H, singlet; the spectrum of the parent amide showed a doublet,  $J$  = 1.8 Hz, at 7.29, 2 H, which was shown to be due to a long range effect of the amide proton, replacement by chlorine removed this interaction). See page 94 for ir and nmr spectra.

## 2. N-Chlorosulfonamides

The N-alkylsulfonamides used as starting materials in these syntheses were mainly prepared according to the general method given by Hinsberg and Kessler:<sup>96</sup> the sulfonyl chloride was added to a solution of the corresponding amine in ca. 10% (by weight) aqueous sodium hydroxide solution at 5-10°. Conversion to the N-chlorosulfonamide was achieved according to the method of Okahara, et al.<sup>76</sup> Chlorine was passed into a suspension of the sulfonamide in an aqueous sodium hydroxide solution (ca. 2.5% by weight) at ice bath temperatures until the yellow color of chlorine persisted. In two cases the method of Neale and Marcus<sup>78</sup> was employed, utilizing tert-butylhypochlorite as a chlorinating agent. However, as much longer reaction times were required in the latter method, a preference was given to the synthetic route of Okahara, et al.<sup>76</sup>

The same spectroscopic methods as used in the syntheses of the N-chloroamides was employed in the identification of the N-chlorosulfonamides which, however, showed an enhanced instability at higher temperatures and could generally not be purified by distillation. N-Chloro-N-methylmethanesulfonamide. The synthesis of the starting N-methylmethanesulfonamide was achieved in 45% yield from 22.9 g (0.20 mol) methanesulfonyl chloride (commercially available) and 18.6 g (0.60 mol) monomethylamine according to the procedure of Baxter, et al.<sup>97</sup> A solution of the amine in 150 ml dry ether was cooled to -10° with an ice/ammonium chloride bath, the solution of the sulfonyl chloride was added very slowly to keep the temperature below -5°. After complete addition the reaction mixture was gradually

warmed to room temperature, stirred for an additionally three hours and filtered from the precipitate which was washed with ether and chloroform. After removal of these solvents by distillation the product was distilled: bp 110-114°, 0.25 mm (lit.<sup>97</sup> 117-118°, 0.3 mm).

Conversion to the N-chloro compound was achieved in 47% yield according to the procedure of Okahara, et al.:<sup>76</sup> bp 62-64°, 1mm (lit.<sup>79</sup> 64-65°, 1 mm).

N-Chloro-N-ethylmethanesulfonamide. The parent sulfonamide was synthesized in 66% yield from 11.4 g (0.10 mol) methanesulfonyl chloride and 13.5 g (0.30 mol) monoethylamine using the same procedure as had been described for the synthesis of N-chloro-N-methylmethanesulfonamide: bp 108-111°, 0.25 mm (lit.<sup>98</sup> 105.5-107.0°, 0.3 mm).

Conversion to the N-chlorosulfonamide was achieved in the previously described manner. No distillation was attempted since N-chloro-N-tert-butylmethanesulfonamide was known to decompose at higher temperatures.<sup>78</sup> The product was dried over 4 Å molecular sieves: ir (CHCl<sub>3</sub>) 7.4 and 8.6 μ (-SO<sub>2</sub>-N=); nmr (CDCl<sub>3</sub>) τ 8.65 (3 H, triplet, J = 7.0 Hz), 6.93 (3 H, singlet), 6.48 (2 H, quartet, J = 7.0 Hz). See page 96 for ir and nmr spectra.

N-Chloro-N-iso-propylmethanesulfonamide. N-iso-propylmethanesulfonamide was synthesized according to the method of Baxter, et al.,<sup>97</sup> in 81% yield from 17.2 g (0.15 mol) methanesulfonyl chloride and 26.6 g (0.45 mol) iso-propylamine: mp 33° (lit.<sup>99</sup> 34-35°). Synthesis of the corresponding N-chlorosulfonamide was achieved in the previously described manner; no distillation was attempted: ir (CCl<sub>4</sub>) 7.4 and 8.5 μ (-SO<sub>2</sub>-N=); nmr (CDCl<sub>3</sub>) τ 8.72 (6 H, doublet, J = 6.0

Hz), 6.92 (3 H, singlet), 5.60 (1 H, septet,  $J = 6.0$  Hz). See page 98 for ir and nmr spectra.

N-Chloro-N-tert-butylmethanesulfonamide. The synthesis of the parent amide was achieved in 33% yield from 16.0 g (0.14 mol) methanesulfonyl chloride and 8.0 g (0.11 mol) tert-butylamine according to the procedure of Hinsberg and Kessler:<sup>96</sup> mp 43° (lit.<sup>96</sup> 40-41°).

N-Chloro-N-tert-butylmethanesulfonamide was prepared in 17% yield from 3.9 g (0.026 mol) N-tert-butylmethanesulfonamide and 3.8 g (0.035 mol) tert-butylhypochlorite following the method given by Neale and Marcus.<sup>78</sup> A distillation was not attempted since these workers reported decomposition of the N-chloro compound at 88°, 1 mm.

N-Chloro-N-iso-propylphenylsulfonamide. N-iso-propylphenylsulfonamide was prepared in 36% yield from 38.8 g (0.20 mol) benzenesulfonyl chloride (commercial reagent) and 17.7 g (0.30 mol) iso-propylamine according to the procedure given by Hinsberg and Kessler:<sup>96</sup> bp 187-191°, 15 mm (lit.<sup>100</sup> 190°, 13 mm). The synthesis of the N-chloro compound was achieved in 49% yield from 5.4 g (0.027 mol) N-iso-propylphenylsulfonamide utilizing the method of Okahara, et al.<sup>76</sup> The ir and nmr spectra showed similar features as the ones obtained from N-chloro-N-iso-propylmethanesulfonamide. Further purification by distillation was not attempted to avoid decomposition at higher temperatures.

N-Chloro-N-tert-butylphenylsulfonamide. The parent sulfonamide was synthesized in 82% yield from 14.5 g (0.083 mol) benzenesulfonyl chloride and 4.0 g (0.055 mol) tert-butylamine in the same manner as N-iso-propylphenylsulfonamide: mp 80-80.5° (lit.<sup>74</sup> 79-80°). Conver-

sion to the N-chlorosulfonamide was achieved in 62% yield by refluxing 8.2 g (0.039 mol) N-tert-butylphenylsulfonamide and 4.7 g (0.043 mol) tert-butylhypochlorite in 75 ml  $\text{CCl}_4$  in the presence of 0.15 g potassium carbonate for 8 hours according to the method of Neale and Marcus:<sup>78</sup> mp 56-57° (lit.<sup>74</sup> 58°).

N-Chloro-propanesultam. The synthetic route given by Bliss and his coworkers<sup>77</sup> was used in the preparation of propanesultam.

The starting 3-chloro-propylthiolacetate was synthesized by the method of Sjöberg.<sup>101</sup> One hundred grams (1.31 mol) thiolacetic acid were added dropwise to 101 g (1.31 mol) allylchloride in the presence of 2 ml tert-butylperoxide at ice bath temperatures with stirring. After complete addition the reaction mixture was warmed gradually to 60° and stirred at this temperature for 8 hours. The slightly green liquid obtained was distilled at reduced pressure: bp 63-68°, 4 mm (lit.<sup>77</sup> 74-76°, 6 mm).

A 1000 ml three-necked flask was fitted with a stirrer, a thermometer, and gas inlet and outlet tubes. A mixture of 66.5 g (0.36 mol) 3-chloro-propylthiolacetate, 100 ml cold water, and 100 g crushed ice was prepared in this flask which was cooled by an ice bath. Chlorine was passed into the solution at such a rate to keep the temperature between 5-10°. Crushed ice was added as necessary. The color of the reaction mixture turned from bright yellow to pink and then colorless. After about 1.5 hours the yellow color of chlorine persisted. The heavy oil formed was separated and the aqueous solution was extracted twice with ether. The combined oil and ether extracts were washed with water and dried over anhydrous sodium sul-

fate. Filtration and distillation of the ether gave a yellow oil. The crude 3-chloropropanesulfonamide was obtained in 90% yield and converted to the 3-chloropropanesulfonamide without further purification.

A mixture of 400 ml ether and 58 ml (ca. 0.93 mol) concentrated aqueous ammonium hydroxide solution in a 1000 ml flask was cooled to 5°. A solution of 57.0 g (0.315 mol) 3-chloropropanesulfonyl chloride in 200 ml ether was added at such a rate to maintain a temperature of 5-7° in the reaction flask. The ether layer was separated and dried over anhydrous sodium sulfate. Petroleum ether (bp 30-60°) was added until faint turbidity occurred. Upon cooling, 3-chloropropanesulfonamide was collected in 63% yield: mp 61-63° (lit.<sup>77</sup> 63°).

Conversion to the cyclic sulfonamide was achieved in 54% yield according to the procedure of Bliss, et al.<sup>77</sup> To a solution of 31.0 g (0.196 mol) 3-chloropropanesulfonamide in 270 ml absolute ethanol which had been freshly distilled over potassium hydroxide was added a solution of 11.0 g (0.196 mol) potassium hydroxide in 54 ml absolute ethanol. The reaction mixture turned neutral after refluxing for one hour. A solution of 0.5 g KOH in 20 ml absolute ethanol was added and refluxing continued for 30 min. After cooling the basic solution was filtered from a white precipitate which was washed twice with 15 ml portions of ethanol. The filtrate and the washings were combined, neutralized with concentrated hydrochloric acid and filtered again. The ethanol was removed by distillation and the product propanesultam distilled: bp 173-175°, 2 mm (lit.<sup>77</sup> 156-157°, 2 mm).

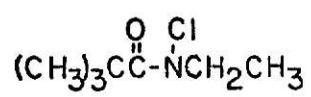
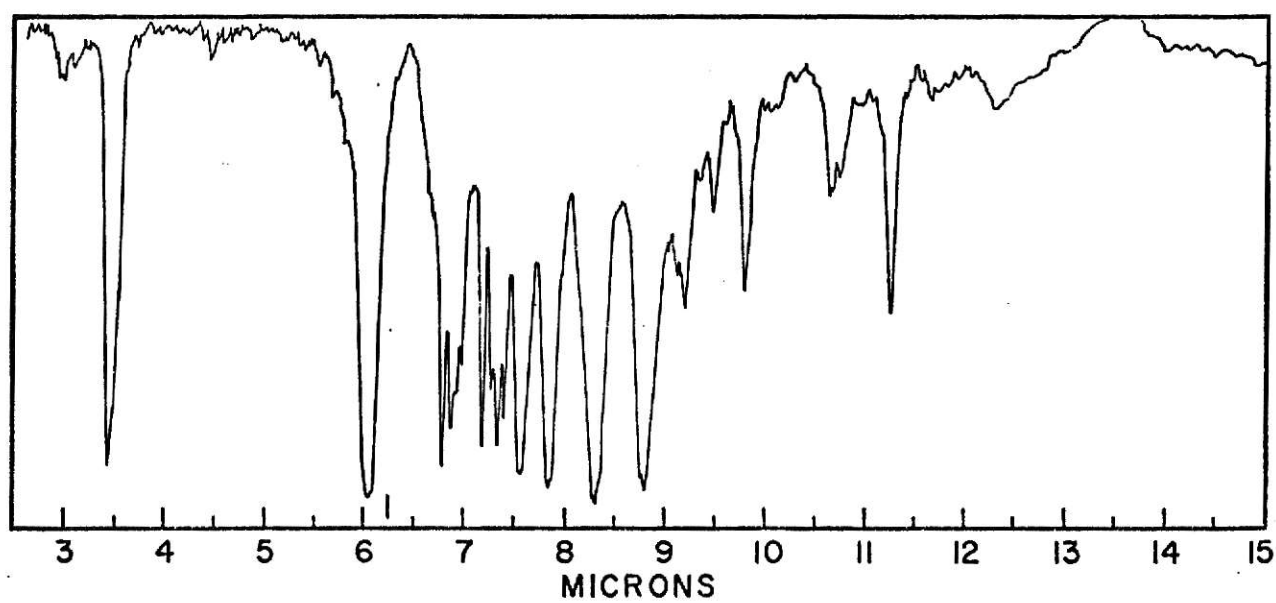
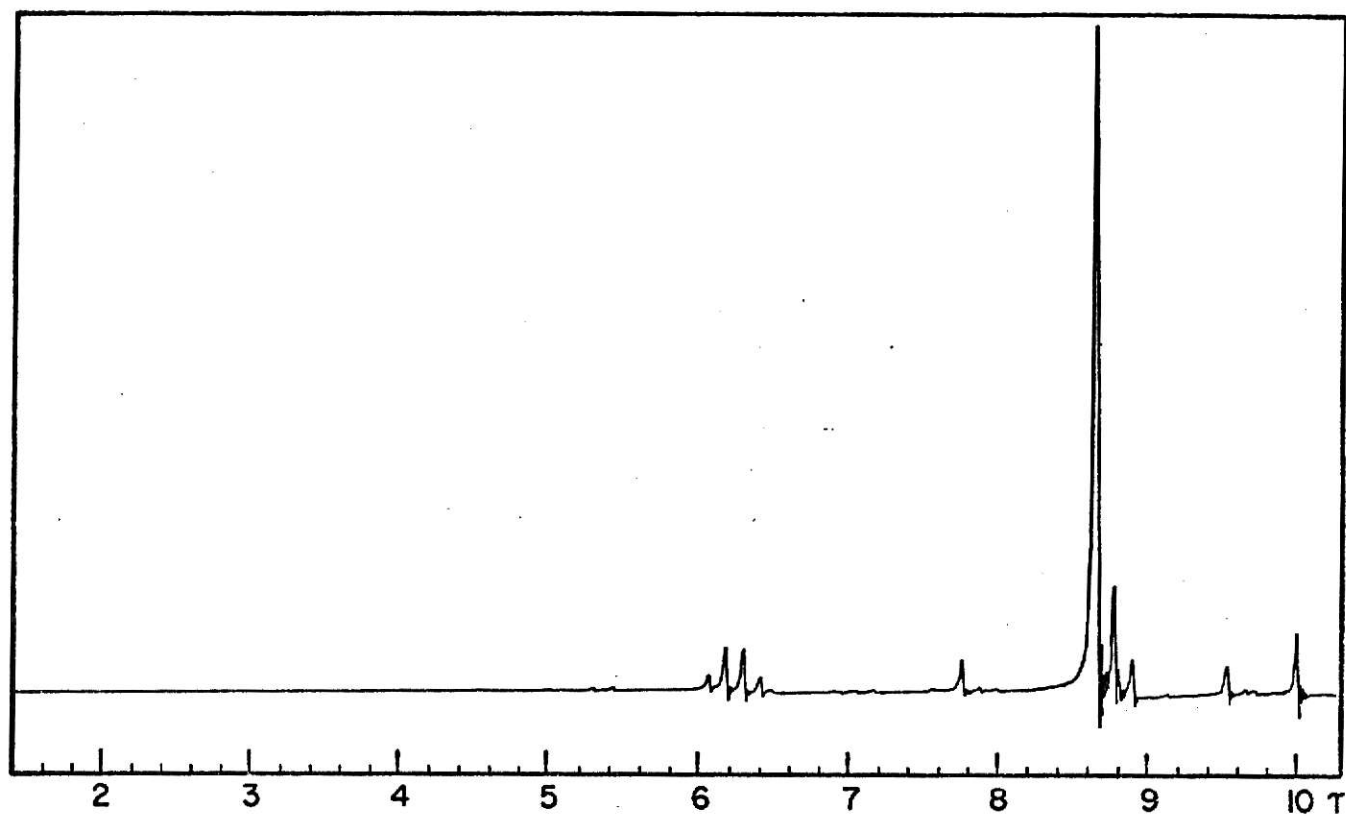
N-Chloro-propanesultam was obtained in 56% yield from 6.0 g (0.049 mol) propanesultam by the method of Okahara, et al.:<sup>76</sup> bp 118-122°, 0.5 mm; ir (neat 7.5 and 8.6  $\mu$  (-SO<sub>2</sub>-N=); nmr (CDCl<sub>3</sub>)  $\tau$  7.40 (2 H, multiplet), 6.55 (4 H, multiplet). See page 100 for ir and nmr spectra.

D. NMR and IR Spectra

N-Chloro-N-ethylpivalamide

NMR ( $\text{CDCl}_3$ , internal TMS)

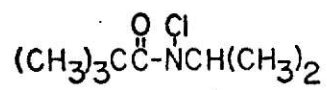
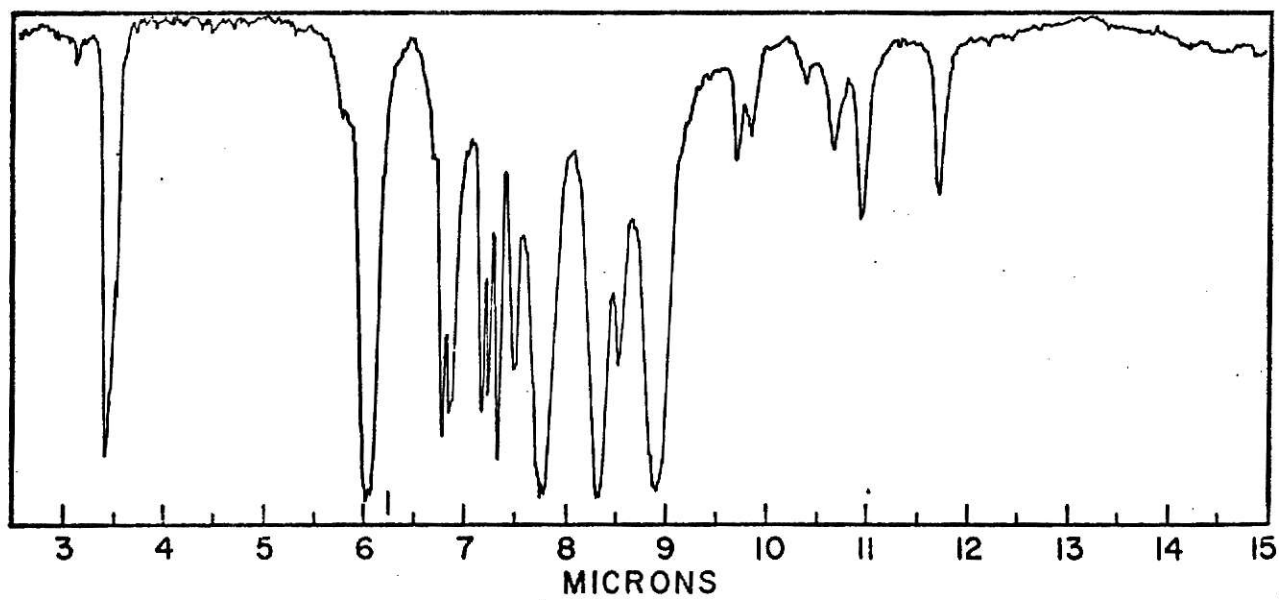
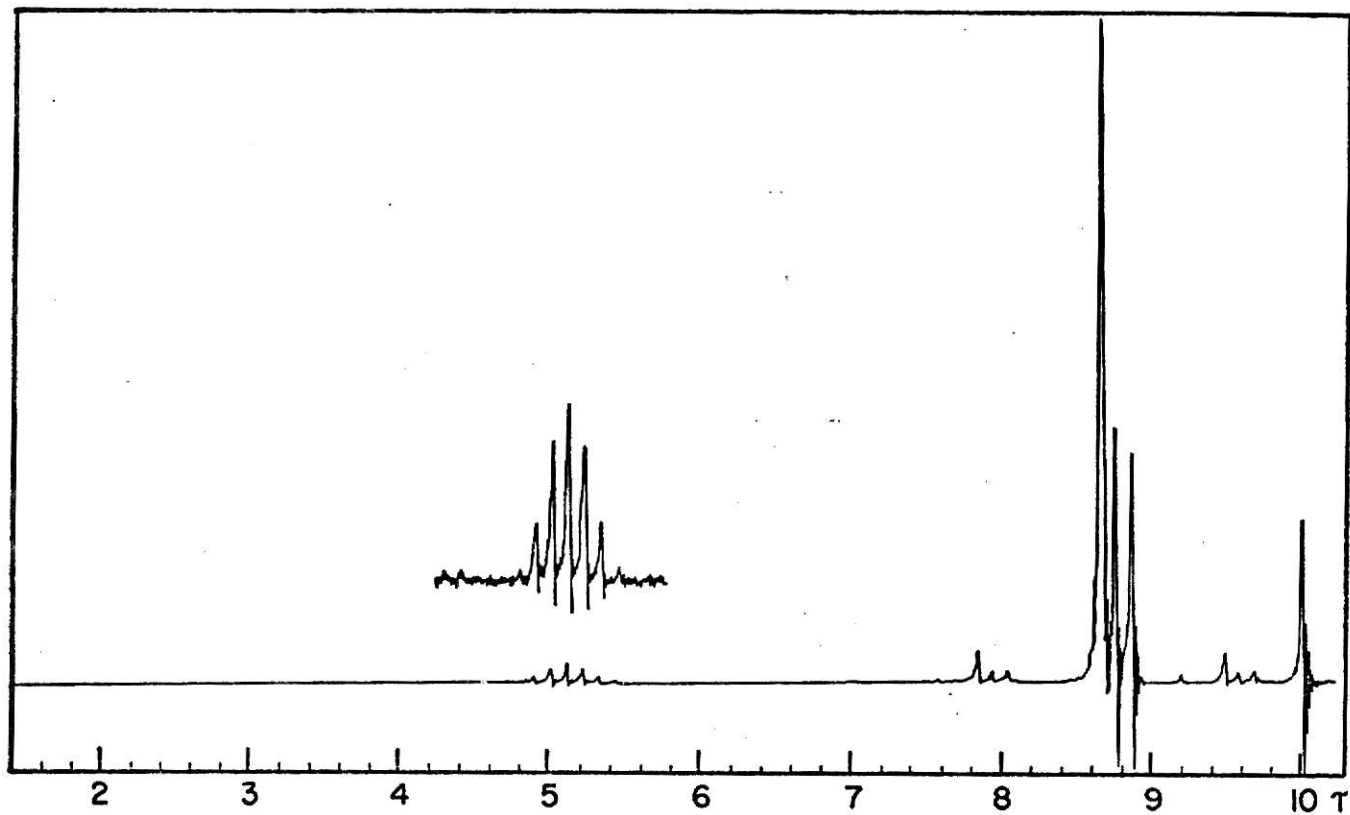
IR ( $\text{CCl}_4$ )



N-Chloro-N-iso-propylpivalamide

NMR ( $\text{CDCl}_3$ , internal TMS)

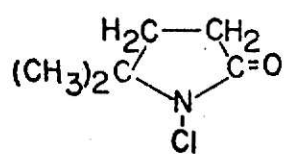
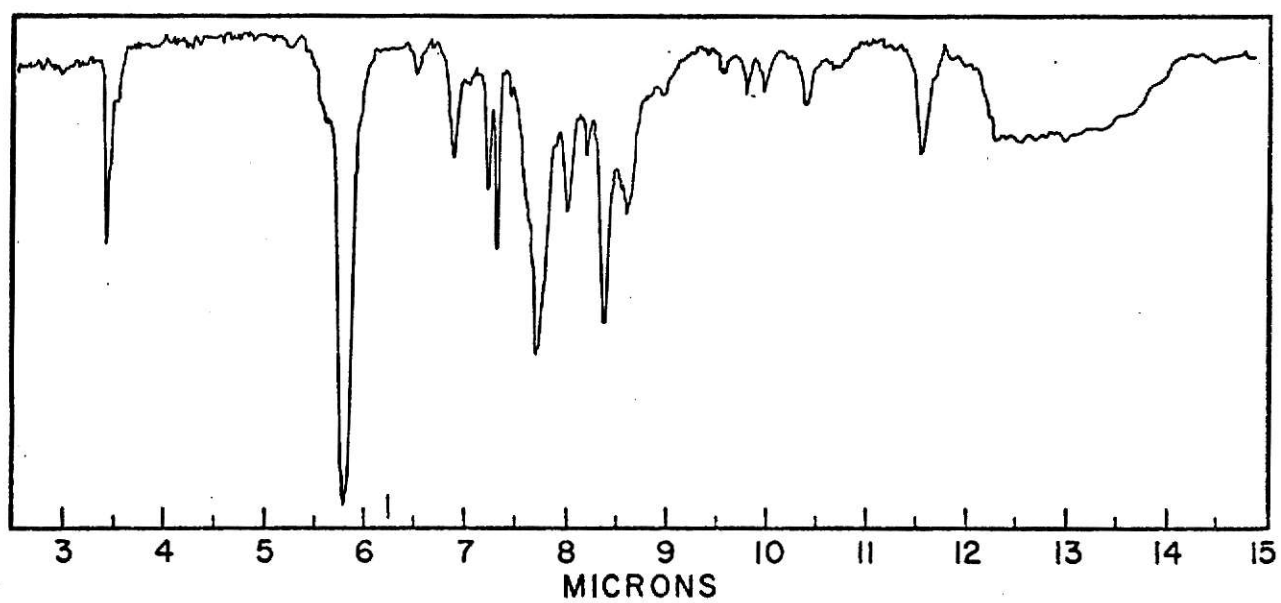
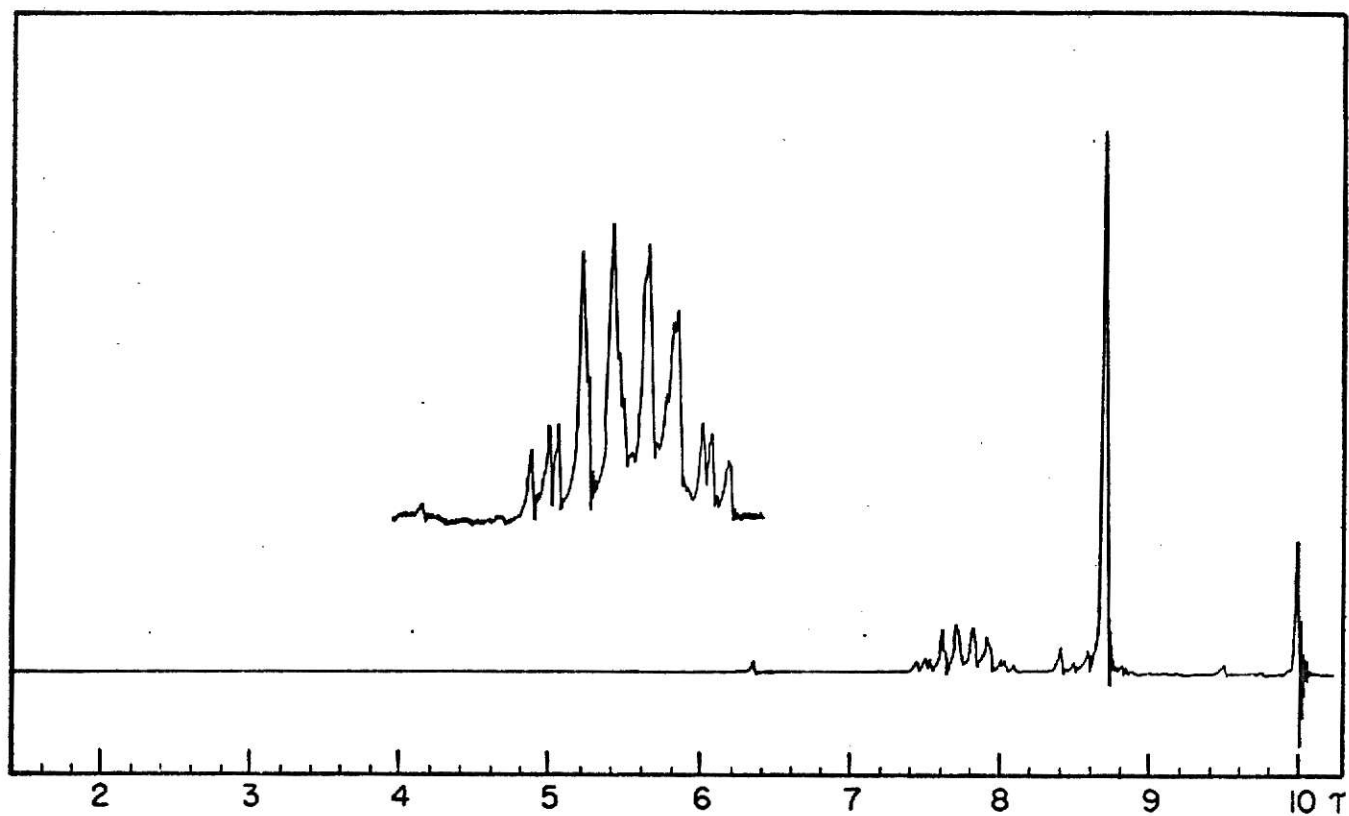
IR ( $\text{CCl}_4$ )



N-Chloro-5,5-dimethyl-2-pyrrolidinone

NMR ( $\text{CCl}_4$ , internal TMS)

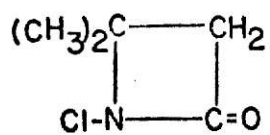
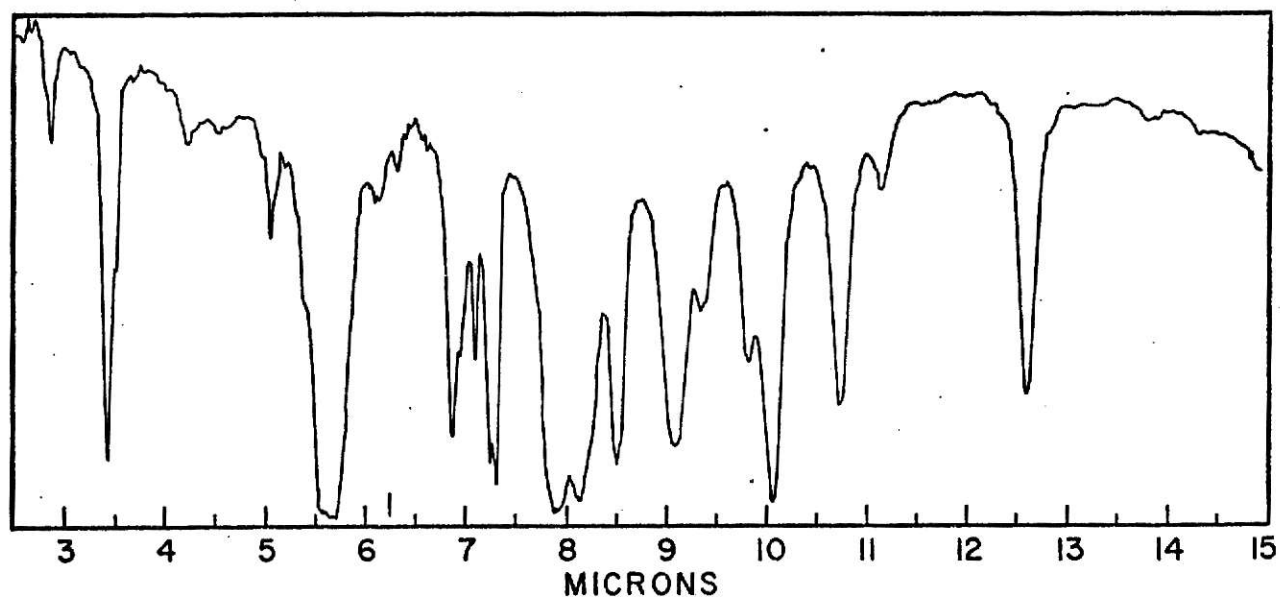
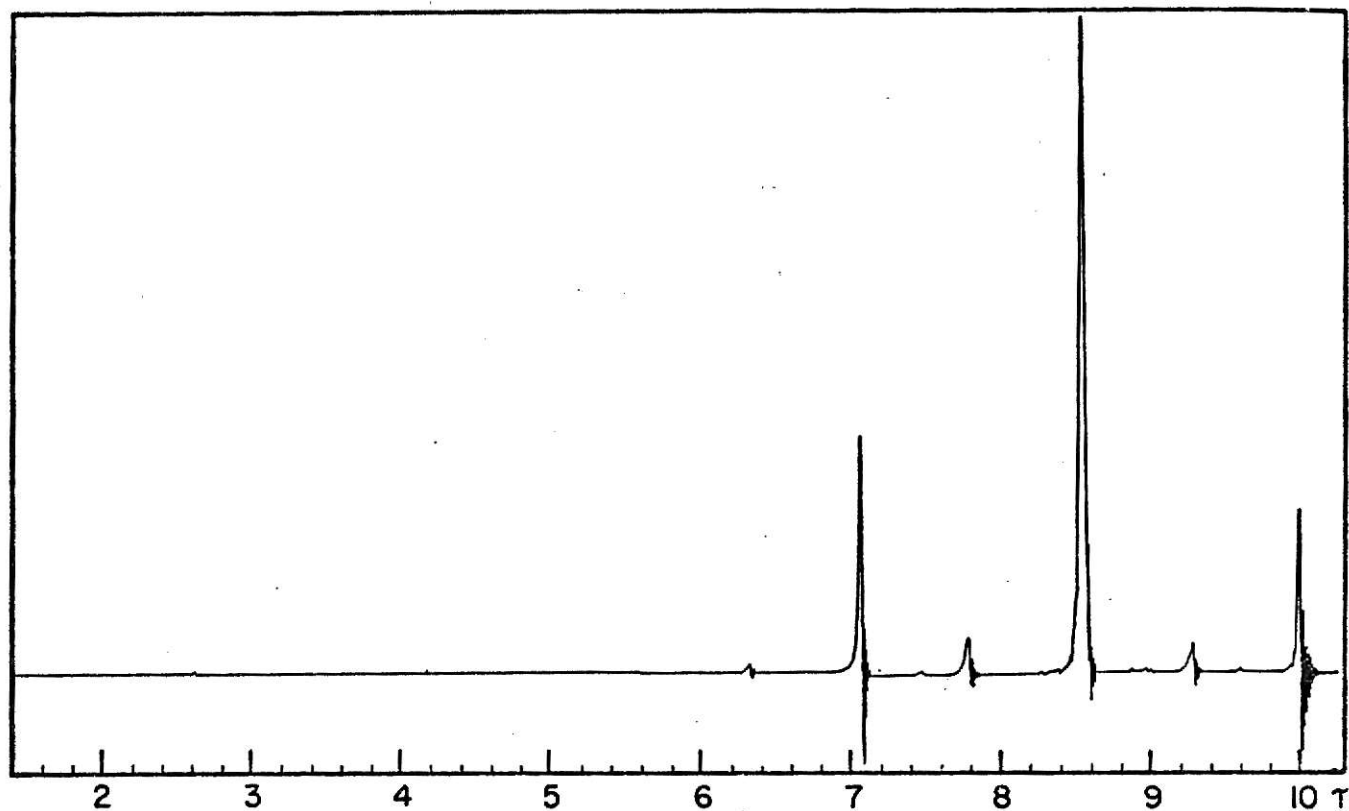
IR ( $\text{CCl}_4$ )



N-Chloro- $\beta$ -iso-valerolactam

NMR ( $\text{CDCl}_3$ , internal TMS)

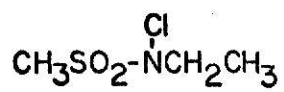
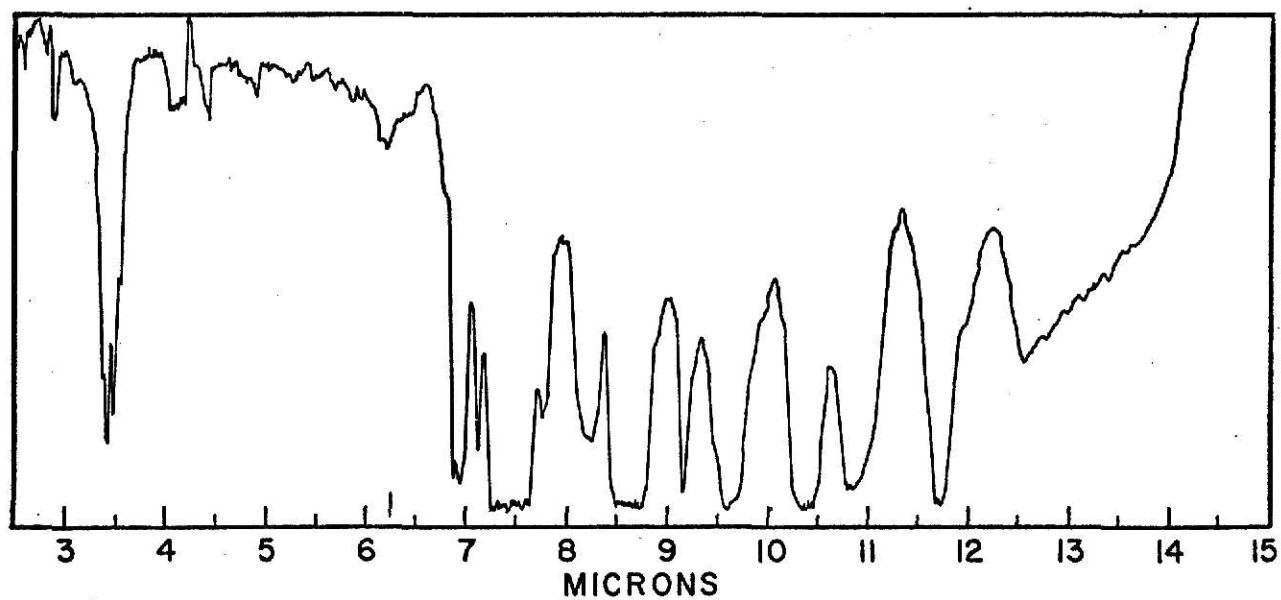
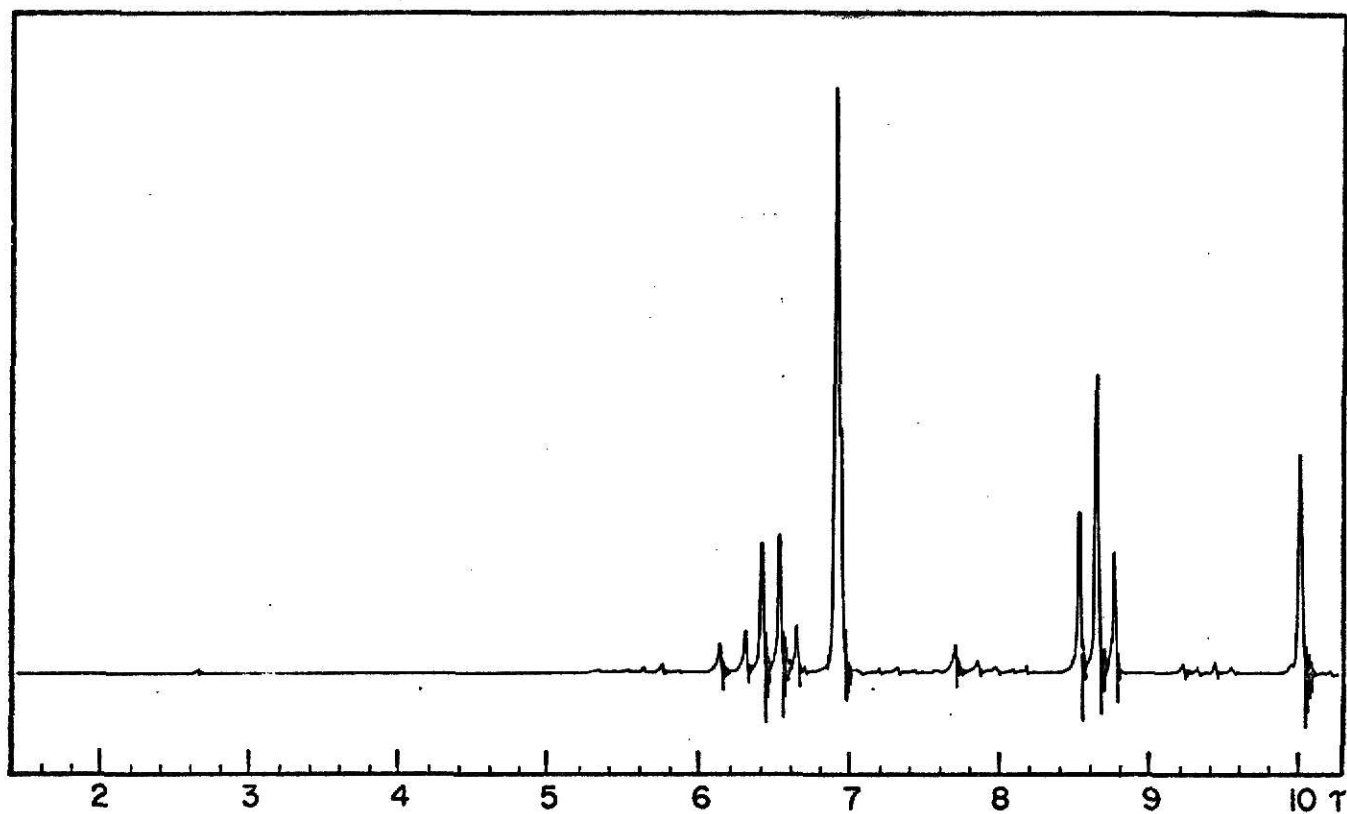
IR (neat)



N-Chloro-N-ethylmethanesulfonamide

NMR ( $\text{CDCl}_3$ , internal TMS)

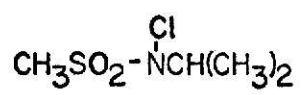
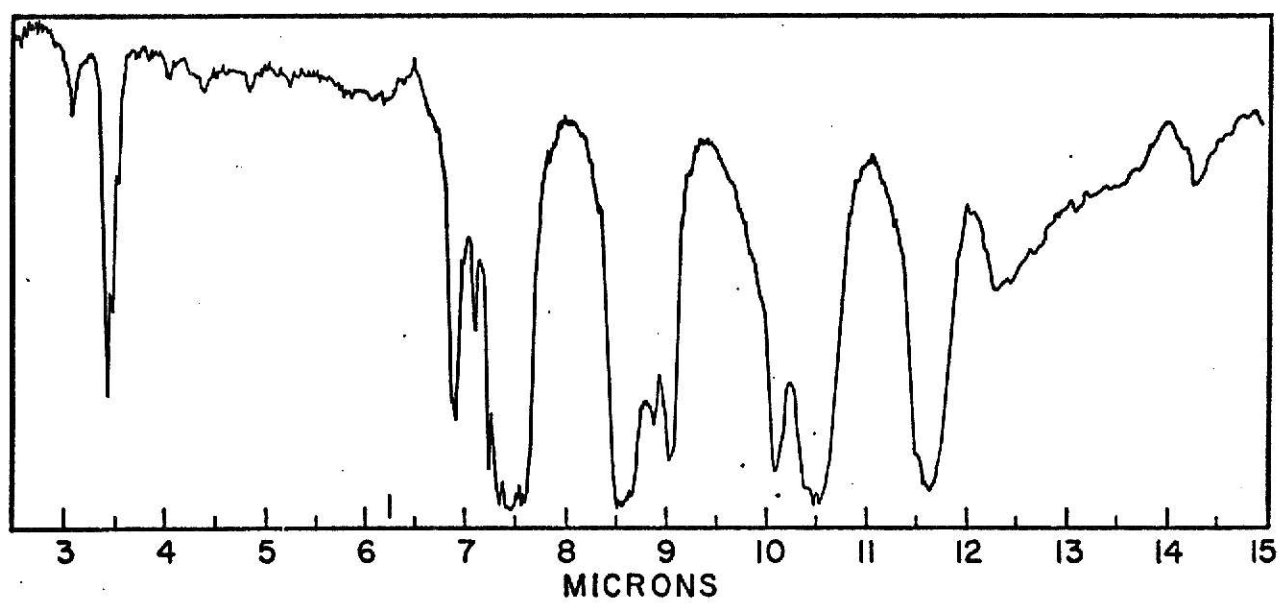
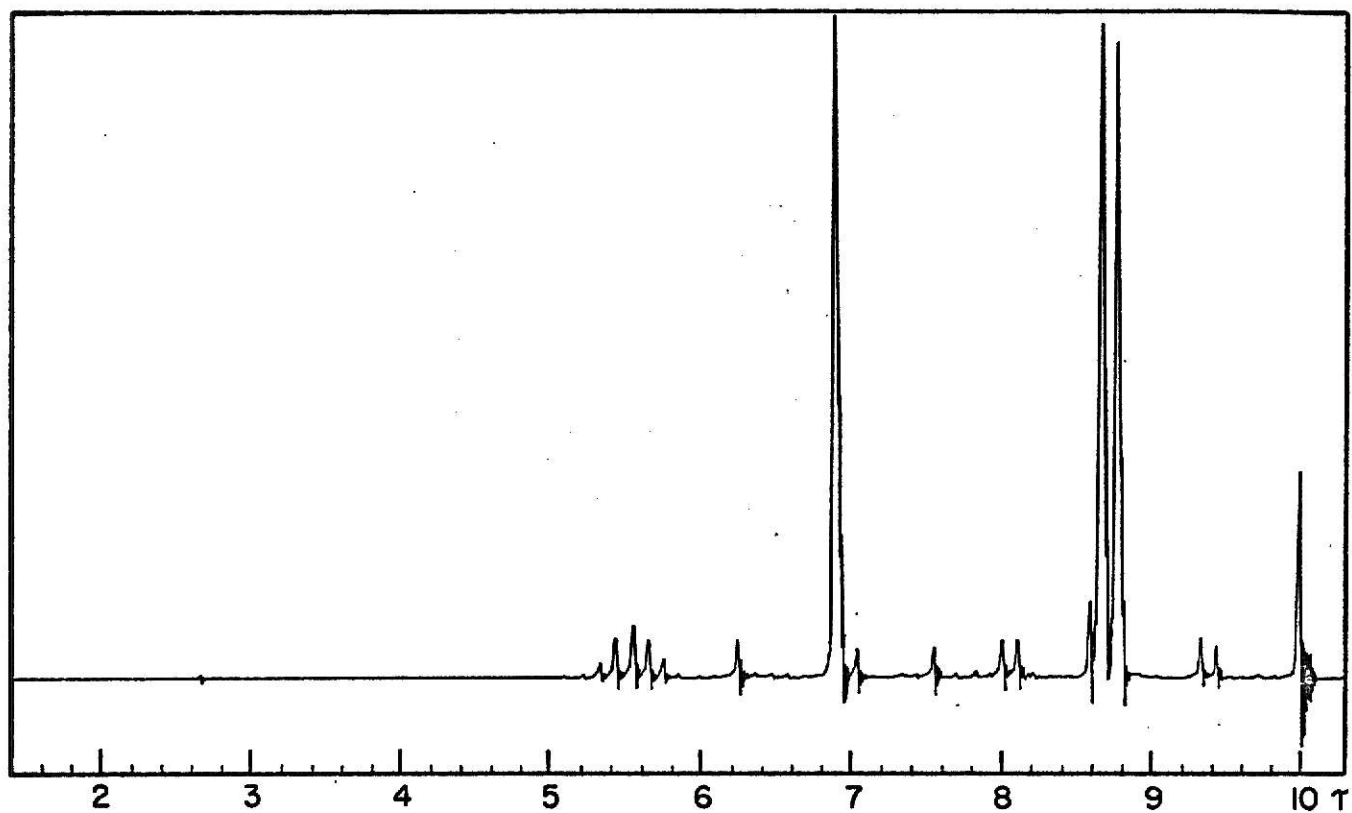
IR ( $\text{CHCl}_3$ )



N-Chloro-N-iso-propylmethanesulfonamide

NMR ( $\text{CDCl}_3$ , internal TMS)

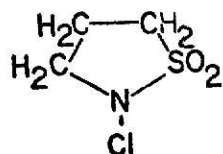
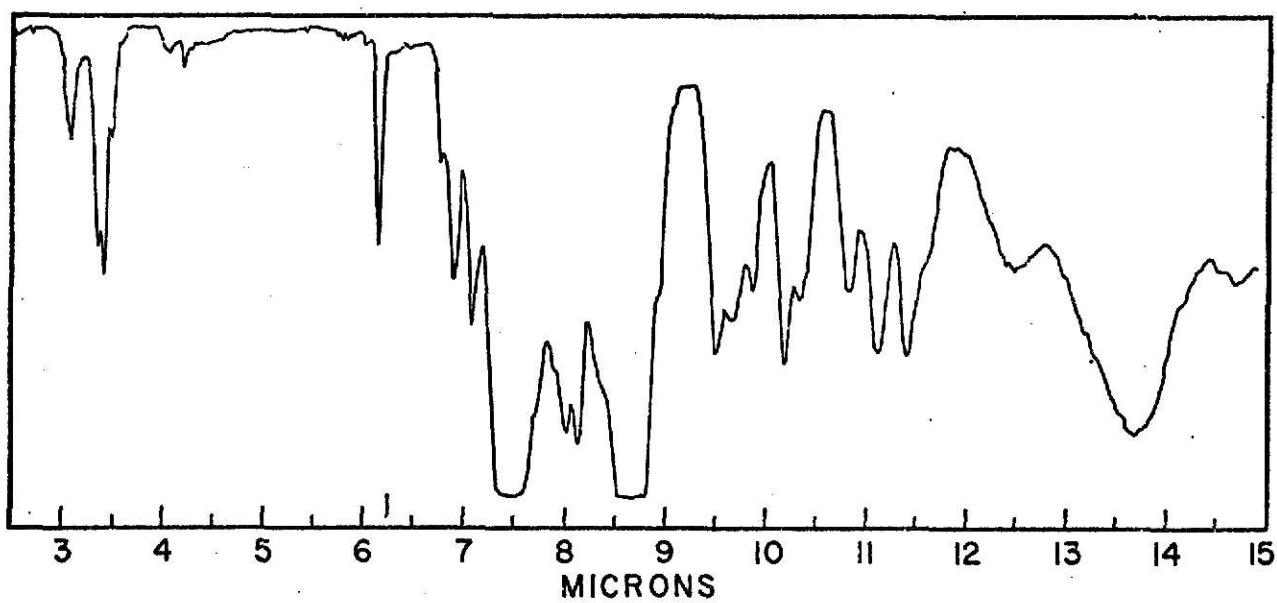
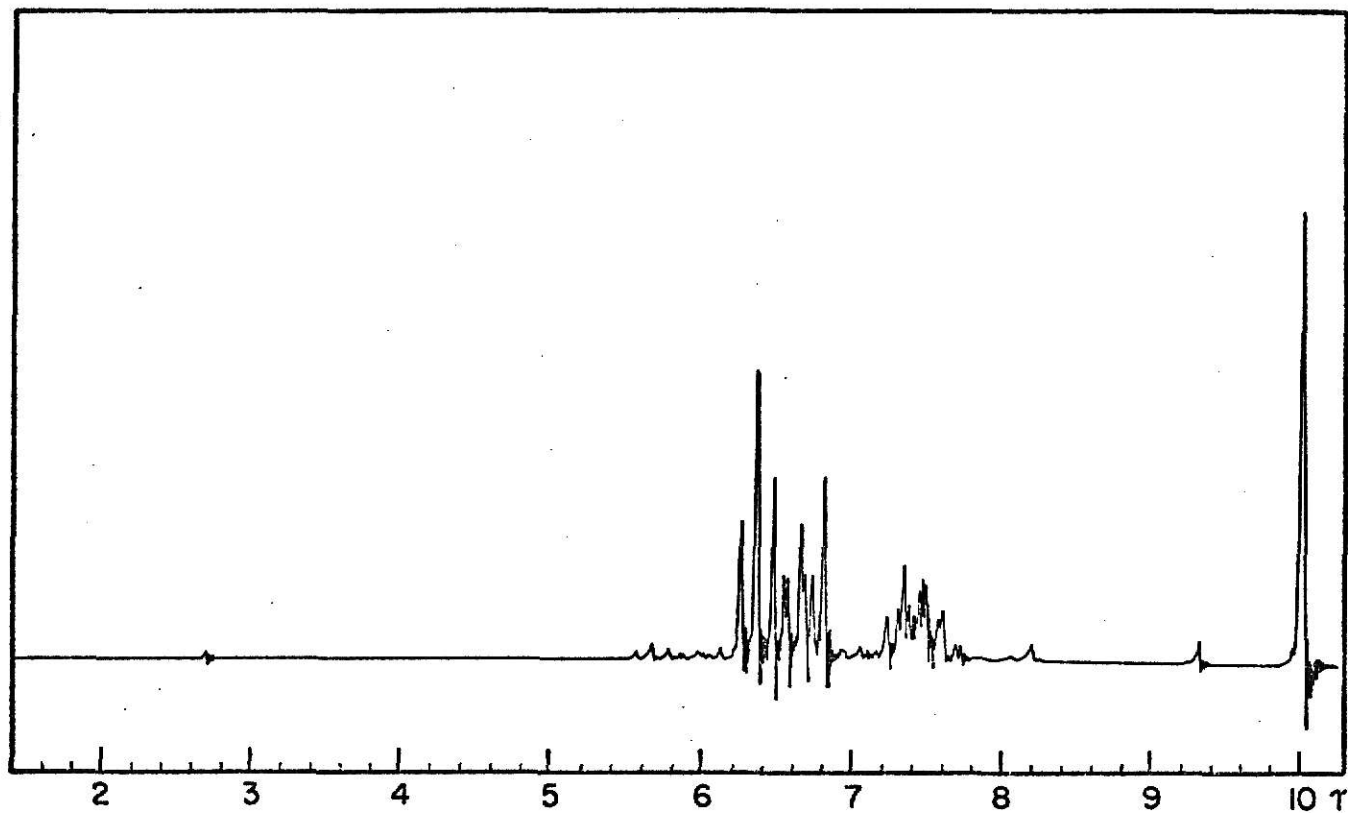
IR ( $\text{CCl}_4$ )



N-Chloropropanesultam

NMR ( $\text{CDCl}_3$ , internal TMS)

IR (neat)



## IV. SUMMARY

It was shown that upon photolysis of N-chloroamides,  $R-C(O)-N(Cl)-R'$ , in cyclopropane at low temperatures directly in the cavity of the esr spectrometer signals of the corresponding amido radicals were detected. Identity of the radicals producing the esr signals was established by comparison with similar radicals reported in the literature. The obtained hyperfine splitting constants (hfsc's),  $a^N$  ca. 15 gauss and  $a_{NCH_3}^H = 29.30$  gauss were interpreted in terms of a II electronic ground state of amido radicals in which the unpaired electron resided in a 2p orbital on nitrogen in conjugation with the  $\pi$ -system of the carbonyl group. The magnitude of the hfsc for the N-methyl protons furthermore suggested that there was not extensive delocalization of the unpaired electron onto the carbonyl group.

X-irradiation of a N-chloroformamide in an adamantane matrix did not produce the expected formamido radical but the carbon-centered formyl radical, instead.

By photolyzing N-chloroamides in air-saturated toluene at low temperatures, spectra of the corresponding acyl nitroxides were observed. The identity of these radicals was evidenced by the mode of generation, the relatively small  $a^N$  and  $a_{NCH_3}^H$  coupling constants, g values characteristic of nitroxides, and comparison with reported acyl nitroxides.

Using the semiempirical INDO method and a systematic population scheme for all orbitals, an energetic preference of ca. 15 kcal/mol

was given to a II electronic configuration of the N-methylformamido radical compared with the  $\sum_N$  state in which the unpaired electron resided in a 2p orbital on nitrogen in the plane of the molecule. However, smaller hfsc's than observed were calculated by the INDO method for a II state due to the overestimate of conjugational effects of the unpaired electron with the carbonyl group.

Analysis of  $\beta$ -hydrogen hyperfine interaction in methyl, ethyl, and iso-propyl substituted amido radicals revealed decided conformational preferences in these radicals by comparison with the corresponding  $\beta$ -hfsc's of dialkylamino radicals and dialkylaminium radical cations. The results suggested that the preferred conformation at the nitrogen site in amido radicals was bent which was taken as further evidence for a II electronic ground state of amido radicals since the INDO method predicted an angle of  $121^\circ$  for the energy-minimized geometry in this particular electronic state. However, the INDO method failed to predict correct conformational preferences in the N-ethylformamido radical due to the overestimate of hyperconjugational effects of the carbon-carbon bond with the unpaired electron. Therefore, a very high potential barrier to rotation of several kcal/mol was predicted. From experimental results it was inferred that interactions of the substituent group with the lone pair of electrons on nitrogen largely determined the preferred time-averaged conformation and interactions with the unpaired electron were secondary in nature.

Upon photolysis of N-chlorolactams in solution no esr signals were recorded. However, spin trapping experiments indicated that

homolytic cleavage of the N-Cl bond was the initial photolytic reaction. The g values of spectra of these cyclic N-chloroamides obtained in an adamantane matrix upon x-irradiation suggested that carbon-centered  $\dot{\text{I}}$  radicals were formed as secondary products, indicating that the cyclic nitrogen-centered radicals were very susceptible to intramolecular abstraction and elimination reactions.

Upon photolysis of N-chlorosulfonamides,  $\text{R-SO}_2\text{-N(Cl)-R'}$ , in cyclopropane at reduced temperatures esr spectra of the corresponding sulfonamido radicals,  $\text{R-SO}_2\text{-}\dot{\text{N}}\text{-R'}$ , were recorded. These radicals exhibited very similar spectral parameters as had been obtained for the corresponding amido radicals. Therefore, a  $\text{II}$  electronic configuration was also suggested for sulfonamido radicals. The dependence of the  $\beta$ -hydrogen hfsc's on the alkyl substitution at the nitrogen site likewise revealed a bent S-N-C geometry and a restricted rotation about the N-C bond, a result that was confirmed from temperature dependence studies of the  $\beta$ -hydrogen hfsc of the N-iso-propylsulfonamido radical.

Esr evidence for a cyclic nitrogen-centered sulfonamido radical was obtained upon photolysis of N-chloropropanesultam in cyclopropane. The result indicated that open chain and cyclic amido radicals were of the same electronic configuration.

Sulfonyl nitroxides,  $\text{R-SO}_2\text{-N}(\dot{\text{O}})\text{-R'}$ , were obtained under similar experimental conditions as were employed for the generation of acyl nitroxides, a result which emphasized the similarity of the nitrogen-centered radicals derived from N-chloroamides and -sulfonamides.

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## VI. ACKNOWLEDGMENTS

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Kansas State University Bureau of General Research for support of this work. Thanks are also due to Kansas State University for assistance in defraying computing costs.

Appreciation is expressed to Dr. Danen for his expert guidance and inspiration during the course of this research.

I would also like to express my appreciation to the Chemistry Faculty and my colleagues at Kansas State University for many helpful suggestions. Special note is made to Dr. West who aided me in many details regarding the esr experiments and offered many helpful suggestions.

To my wife, my deepest appreciation for her sacrifices and patience. And I am very thankful to my parents who gave all for my education.

## VII. VITA

The author was born January 6, 1947 in Leipzig, Germany. After his parents moved to the western part of this country, the author obtained his high school "Abitur" at Hittorf Gymnasium, Recklinghausen, in 1966. After two years in the service, the author started the study of chemistry at Justus-Liebig Universitaet, Giessen, West Germany, in April 1968. Three years later the author entered the academic exchange program of Justus-Liebig Universitaet and Kansas State University and continued his graduate study in the field of chemistry at Kansas State University in August 1971.

The author is married and he and his wife have one girl, born March 11, 1973.

The author is a member of the American Chemical Society and Phi Lambda Upsilon.

ELECTRON SPIN RESONANCE STUDIES OF  
TRANSIENT AMIDO AND SULFONAMIDO FREE RADICALS

by

ROLAND WERNER GELLERT

Diplom-Chemiker-Vorpruefung, 1970  
Justus-Liebig Universitaet, Giessen

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

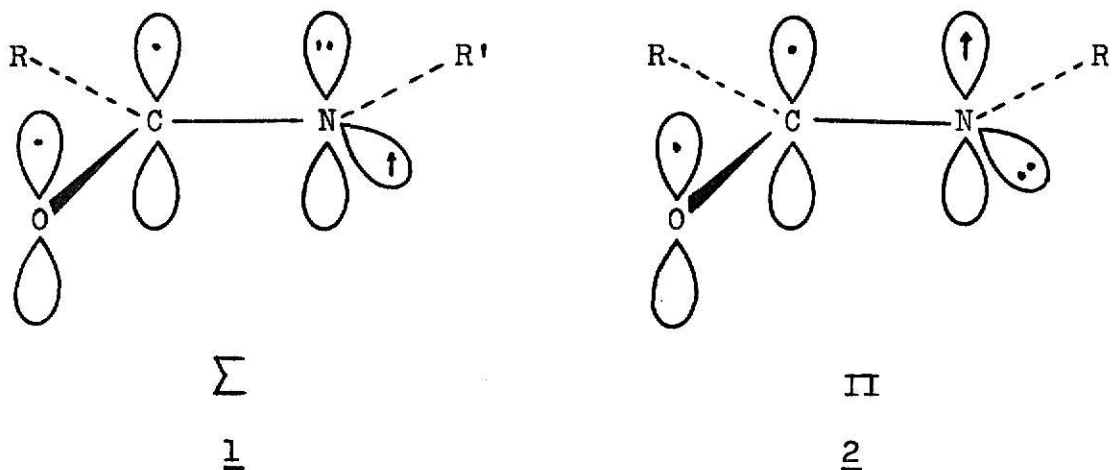
Department of Chemistry

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1973

# ABSTRACT

Amido radicals,  $R-C(O)-\dot{N}-R'$ , had been the subject of considerable controversy due to the possibility of either a  $\Sigma$  or a  $\Pi$  electronic ground state configuration for this type of a radical (cf. 1 and 2).



Purported evidence for both a  $\Pi$  and a  $\Sigma$  structure had been reported in the literature but frequently misassignments of electron spin resonance (esr) spectra occurred.

It was shown in this work that upon photolysis of N-chloroamides,  $R-C(O)-N(Cl)-R'$ , in cyclopropane solutions at low temperatures directly in the cavity of the esr spectrometer, signals of the corresponding amido radicals were detected. The obtained hyperfine splitting constants (hfsc's) for nitrogen and  $\beta$ -protons were interpreted in terms of a  $\Pi$  electronic ground state of amido radicals. The magnitude of the hfsc for the N-methyl protons furthermore suggested that there was not extensive delocalization of the unpaired electron onto the carbonyl group.

X-irradiation of a N-chloroformamide in an adamantane matrix did not produce the expected amido radical but the carbon-centered  $\Sigma$  formyl radical instead.

By photolyzing N-chloroamides in air-saturated toluene solutions, spectra of the corresponding acyl nitroxides,  $R-C(O)-N(\dot{O})-R'$ , were obtained.

Using the semiempirical intermediate neglect of differential overlap (INDO) calculations and a systematic population scheme for all valence electrons, an energetic preference of ca. 15 kcal/mol was given to a  $\Pi$  electronic configuration of the N-methylformamido radical compared with the  $\Sigma$  state. Smaller hfsc's than observed were calculated for a  $\Pi$  state due to the overestimate of conjugational effects of the unpaired electron with the  $\pi$ -system of the carbonyl group.

Analysis of  $\beta$ -hydrogen hyperfine interaction in methyl, ethyl, and iso-propyl substituted amido radicals revealed decided conformational preferences in amido radicals. The results suggested that the preferred conformation at the nitrogen site in amido radicals was bent which was taken as further evidence for a  $\Pi$  electronic ground state since the INDO method predicted an angle of  $121^\circ$  for the energy-minimized geometry in this particular electronic state. However, the INDO method failed to predict correct conformational preferences in the N-ethylformamido radical due to the overestimate of hyperconjugational effects of the carbon-carbon bond with the unpaired electron. From experimental results it was inferred that interactions of the substituent group with the lone pair of elec-

trons on nitrogen largely determined the preferred time-averaged conformation.

Upon photolysis of N-chlorolactams no esr signals were recorded. Spin trapping experiments indicated that homolytic cleavage of the N-Cl bond was the initial photolytic reaction. The g values of spectra of these cyclic amides obtained upon x-irradiation in an adamantane matrix suggested that carbon-centered II radicals were formed as secondary products, indicating that the cyclic nitrogen-centered radicals were very susceptible to intramolecular abstraction and elimination reactions.

Upon photolysis of N-chlorosulfonamides,  $R-SO_2-N(Cl)-R'$ , in cyclopropane esr spectra of the corresponding sulfonamido radicals,  $R-SO_2-\dot{N}-R'$ , were recorded. These radicals exhibited very similar spectral parameters as had been obtained for the corresponding amido radicals. Therefore, a II electronic configuration was also suggested for sulfonamido radicals. The dependence of the  $\beta$ -hydrogen hfsc's on the alkyl substitution at the nitrogen site likewise revealed a bent S-N-C geometry and a restricted rotation about the N-C bond.

Esr evidence for a cyclic nitrogen-centered sulfonamido radical was obtained upon photolysis of N-chloropropanesultam. The results indicated that open chain and cyclic sulfonamido radicals were of the same electronic configuration.

Sulfonyl nitroxides,  $R-SO_2-N(\dot{O})-R'$ , were observed under similar experimental conditions as were employed in the generation of acyl nitroxides, a result that emphasized the similarity of the nitrogen-centered radicals derived from N-chloroamides and -sulfonamides.