The quantitative methods of analysis used were checked and were generally found to be reliable within ± 10 %.

Acknowledgements. This work is part of an investigation of the mechanism of oxidation with nitric acid supported by the Swedish Council for Applied Research. We are also indebted to Dr. Erik Bengtsson for his kind interest in the work.

Mass spectrometric analyses were performed by Dr. Ragnar Ryhage at Karolinska Institutet, Stockholm. The experimental work was done with the skilful assistance of Mr. Hasse Hansson and of Mr. Tore Elström, who did most of the analytical work. Gas analyses were done by Mr. Olle Kronblad. The English was checked by Dr. K. H. Baggeley.


Received August 17, 1967.

Interpretation of Proton Magnetic Resonance Spectra of α-Amino Acids in Terms of Rotational Isomers

BØRGE BAK and FLEMMING NICOLAISEN

Chemical Laboratory V, University of Copenhagen, Copenhagen, Denmark

α-Amino acids, except glycine, are mixtures of 3 different rotational isomers (I, II, III) generated by rotation about the Cα–Cβ single bond. The life-time of such “rotamers” may be so short that PMR spectra of α-amino acids are effectively averaged at room temperature. In fact, earlier investigators have all agreed that one PMR spectrum is observable per α-amino acid, meaning a rapid interconversion between I, II, and III. In a recent paper Aruldas has analyzed freshly recorded PMR spectra (100 MHz instrumental frequency) of DL-threonine (CH₃-CHOHCH(NH₂)COOH) and DL-valine ((CH₃)₂CHCH₂NH₂COOH) dissolved in D₂O (25°C). Aruldas believes to have observed 2 superimposed spectra in each of these cases. His interpretation is that two of the rotamers, II and III, are separated by a very large barrier while the remaining barriers of the internal rotation potential function are low, causing the interconversions I → II and I → III to be rapid, while II → III is slow. We are unable to see why this is a satisfactory explanation of the alleged occurrence of 2 spectra since the interconversion II → III could still take place rapidly enough via the rotamer I to produce one and only one averaged spectrum per amino acid.

On the experimental side Aruldas’ paper is in disagreement with, for example, the results obtained by Taddei and Pratt, not cited by Aruldas. These authors investigated PMR spectra (at 60 MHz) of DL-threonine and the diastereomeric allo-threonine under experimental conditions (pH, solvent, and temperature) similar to Aruldas’. In separate experiments (as far as can be seen) Taddei and Pratt observed one methyl group spin-doublet for DL-threonine, and one for allo-threonine, the chemical shift difference being 0.12 ppm. At 100 MHz (Aruldas’ experiment) this corresponds to a chemical shift difference of 12 cps. Fig. 2(b) of Aruldas’ paper shows that there is a chemical shift difference between his two recorded methyl doublets of 11.5 cps. There can be little doubt, therefore, that Aruldas’ sample of alleged DL-threonine has been contaminated (to 30–40 %) by the allo isomer. To exclude any doubt (since the spectra of DL-threonine and allo-threonine are only details in the paper by Taddei and Pratt) we have again recorded the PMR spectrum of DL-threonine in D₂O at 60 MHz. The spectrum of the methyl group is a clear-cut doublet (Fig. 1, lines a and b of this paper) in contrast to the triplet to be expected according to Aruldas.

In the case of DL-valine there is no “allo” isomer to complicate matters. Yet, two methyl group spin-doublets were again observed by Aruldas and the spectrum was tentatively interpreted in analogy with DL-threonine. This feature and the re-
behavior of aqueous solutions of these acids is quite similar to what is found for solutions in CF$_3$COOH, even at 220 MHz. Of course, the molecular species in CF$_3$COOH are ions (CH$_3$CHOHCH$_2$NH$_2$COOH) and not “zwitterions” (CH$_3$CHOHCH$_2$NH$_2^+$ COO$^-$) as in water, but this difference would seem less important in stereochemical respect.


Received August 22, 1967.

Organic Selenium Compounds

IV. Esters of Triselenocarboxylic Acid

L. HENRIKSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, Copenhagen, Denmark

As a part of a current investigation at this laboratory of the chemistry of carbon diselendide,$^{1,4}$ we have prepared a series of esters of triselenocarboxylic acid (I—V).

\[
\text{Se} = \text{Se} \quad \text{II} \quad \text{III} \\
\text{Se} = \text{Se} \quad \text{I} \\
\text{Se} = \text{Se} \quad \text{IV} \quad \text{V}
\]