

## 183. Evidence for an Iminium Cation Intermediate and its Non-Oxidative Decarboxylation in a Cerium(IV)-Mediated Oxidative Decarboxylation

Preliminary communication<sup>1)</sup>

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### Summary

Evidence is provided for the occurrence of a non-oxidative decarboxylation in an iminium cation intermediate which is produced in an oxidative decarboxylation induced by cerium(IV).

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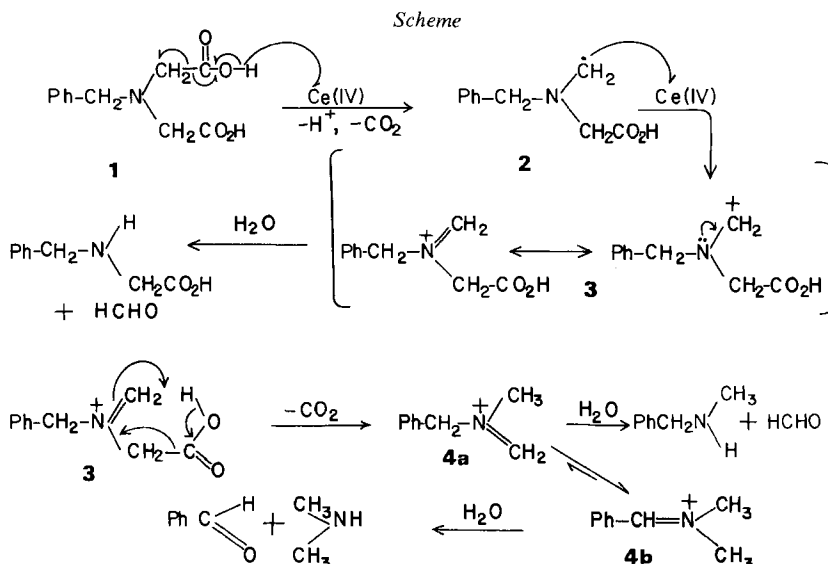
In continuing our investigations of the mechanistic details of metal-ion oxidations of hydroxy acids [1] and amino acids [2], we have now looked into the interaction between cerium(IV) and benzyliminodiacetic acid (BIDA, **1**)<sup>2)</sup>. The reaction of Ce(IV) with BIDA in acidic sulfate or perchlorate media leads to decarboxylation and to the formation of benzaldehyde, formaldehyde, dimethylamine, benzylmethylamine and *N*-benzylglycine<sup>3)</sup>. The Ce(IV)/BIDA stoichiometry is 2:1 as determined by potentiometry. Surprisingly, however, the Ce(IV)/CO<sub>2</sub> ratio is just about unity. If BIDA underwent decarboxylation only by an oxidative pathway one would expect Ce(IV)/CO<sub>2</sub>=2. The observation and the expectation are reconciled readily when one inspects the products portrayed in the *Scheme*. Electron transfer from the carboxyl group of **1** to Ce(IV) initiates decarboxylation and leads to the formation of a free radical (**2**)<sup>4)</sup>. The free radical loses an electron

<sup>1)</sup> A more detailed communication is planned for publication at a later date.

<sup>2)</sup> We chose BIDA for two reasons: (a) BIDA is the major structural unit of Chelex 100, a chelating ion-exchange resin used frequently in our laboratory and we needed the information regarding its stability towards metal-ion oxidants; (b) The benzene ring in BIDA allows us to vary the electron density systematically at the N-atom in **1** and thereby study the correlation of structure and reactivity; see *S.B. Hanna, J.T. Fenton & M. Moehlenkamp* in 'Correlation Analysis in Organic Chemistry', EUCHEM Conference, Assisi (Italy), Sept. 10-14, 1979.

<sup>3)</sup> The techniques used for separation and identification of the products are summarized here. Benzaldehyde: extraction, GC./MS., m.p. and IR. of 2,4-DNP-derivative; formaldehyde: chromotropic acid, m.p. and IR. of 2,4-DNP-derivative; dimethylamine and benzylmethylamine: TLC. on silica and GC. on Chromosorb 103; *N*-benzylglycine: TLC. on silica.

<sup>4)</sup> Polymerization to a solid gel occurred very shortly after mixing acrylamide, Ce(IV) and BIDA in aqueous solution. Cerium(IV) does not induce polymerization of acrylamide in the absence of BIDA.



rapidly to another Ce(IV) thereby producing a resonance-stabilized *Mannich*-type iminium-cation intermediate (3). The intermediate 3 is capable of undergoing decarboxylation or hydrolysis (see *Scheme*). The product of decarboxylation (4a) undergoes an  $\alpha, \gamma$ -proton shift to 4b to attain stability by establishing conjugation with the aromatic ring. Indeed, it is difficult to account for the formation of benzaldehyde and dimethylamine without the intermediacy of a prototropically-labile 4a. The alternative route of having benzaldehyde from a rearranged 3 is ruled out because of the absence of sarcosine among the reaction products.

The non-oxidative decarboxylation of 3 is reminiscent of pyridoxal-mediated decarboxylations of  $\alpha$ -amino acids [3]. Intermediates similar to 3 have been invoked in the carbonyl-assisted decarboxylation of sarcosine [4].

This duality in decarboxylation pathways is also observed in the Ce(IV)-methyliminodiacetic acid reaction<sup>5</sup>) and may prove to be generally true for Ce(IV) oxidations of aminopolycarboxylic acids. Work is in progress to test such a generalization.

#### REFERENCES

- [1] S. B. Hanna & S. Sarac, *J. Org. Chem.* **42**, 2063 (1977).
- [2] S. B. Hanna, R. K. Hessley & L. M. Nicholson, *Inorg. Chim. Acta* **25**, L7-L8 (1977).
- [3] M. H. O'Leary in E. E. van Tamelen, 'Bioorganic Chemistry', Vol. I, Academic Press, New York, 1977, 259-275; H. C. Dunathan in A. Meister, 'Advances in Enzymology', Vol. 35, Wiley-Interscience Publishers, New York 1971, 79-134.
- [4] G. P. Rizzi, *J. Org. Chem.* **35**, 2069 (1970).

<sup>5</sup>) The Ce(IV)/CO<sub>2</sub> ratio here is just about unity and dimethylamine was detected by GC. and confirmed by m.p. and IR. of the phenylthiourea derivative.