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

Preliminary communication[1]

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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).

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**)[2]. 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[3]. The Ce(IV)/BIDA stoichiometry is 2:1 as determined by potentiometry. Surprisingly, however, the Ce(IV)/CO_2 ratio is just about unity. If BIDA underwent decarboxylation only by an oxidative pathway one would expect Ce(IV)/$CO_2 = 2$. 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**)[4]. The free radical loses an electron

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[1] A more detailed communication is planned for publication at a later date.

[2] 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.

[3] 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.

[4] 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.

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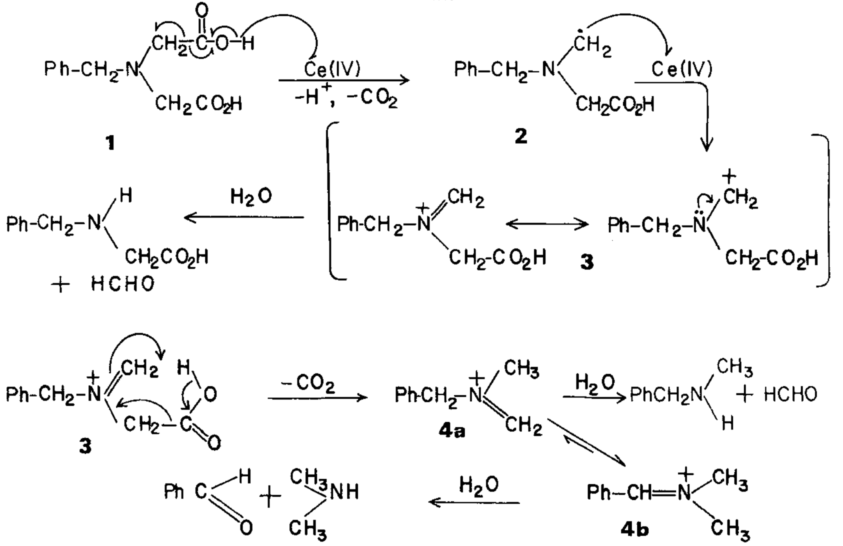
Scheme



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 α,γ-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 α-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[5]) 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).

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[5]) The Ce(IV)/CO_2 ratio here is just about unity, and dimethylamine was detected by GC. and confirmed by m.p. and IR. of the phenylthiourea derivative.