Bredt's Rule: An Anomalous Decarboxylation

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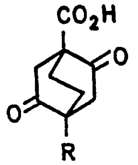
Summary Since the thermal monodecarboxylation of (+)-bicyclo[2,2,2]octan-2,5-dione-1,4-dicarboxylic acid is found to proceed with racemisation, the mechanism cannot involve a bridgehead double bond and so does not infringe Bredt's Rule.

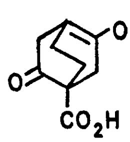
The long-standing report[1] that thermal decarboxylation of (I) yields (II) is currently of great interest, for the intermediate enol (III) envisaged in the Westheimer decarboxylation mechanism[2] (IV) embodies a *trans*-cyclohexene. Such an "anti-Bredt" intermediate was judged to be energetically unattainable in a recent re-statement of the rule,[3] and much evidence[4] supports this conclusion. However, the recent trapping of (V),[5] which is also a *trans*-cyclohexene, refocuses interest on the decarboxylation. We report on a re-examination of the reaction.

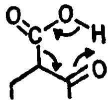
The structure of the decarboxylation product was confirmed by the following synthesis. The bis-acetal (VI) was half-hydrolysed to (VII) and transformed *via* (VIII) (Hunsdiecker reaction) to (IX). Hydrolysis yielded (II), identical with the decarboxylation product.

Significantly, neither (II) nor (X) (synthesised by an unexceptional route) could be decarboxylated, even under forcing conditions. These observations suggested that straightforward Westheimer-type decarboxylation could not explain the reaction (I) → (II).

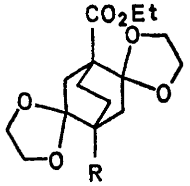
The fact that (III) cannot be an intermediate was established as follows. Optically active diacid (I), $[\alpha]_D = +23{\cdot}3^\circ$, was transformed into (II), by thermal decarboxylation and also by the chemical route [(VI) → (VIII) → (II)] described above. Compared as their methyl esters, the former product showed no significant circular dichroism whilst the latter showed a clearly-defined maximum ($\Delta\epsilon = +0{\cdot}21$) at 292 nm; *i.e.* the decarboxylation proceeds with racemisation.

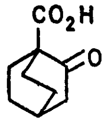

(I): R = CO_2H
(II): R = H


(III)


(IV)


(V)


(VI): R = CO_2Et
(VII): R = CO_2H
(VIII): R = Br
(IX): R = H


(X)

These results are incompatible with the route (I) → (III) → (II) and with a special modification of this route recently suggested.[6] Racemisation must be associated with reversible cleavage of the C_1–C_2 bond to give a planar monocyclic intermediate. Presumably this cleavage occurs on heating (I), (II), and (X), but only in the case of (I) does such an intermediate contain a β-keto acid function, which can undergo normal Westheimer decarboxylation.

Consequently the decarboxylation does not involve a bridgehead double bond, as has been assumed, and does not infringe Bredt's Rule. Subject to the qualification imposed by the authors,[5] (V) remains the most strained bridgehead double bond yet detected, and the sole example which incorporates a *trans*-cyclohexene.

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[4] Ref. 3, Table 1.
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