

A [15]ANNULENONE-[15]ANNULENYL ION CYCLE DRIVEN BY PROTON GRADIENT

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A [15]annulenone-[15]annulenyl ion cycle driven by proton gradient was described. The cycle converts formally proton gradient into free energy through the following four step sequence.

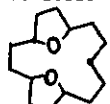
- (i) Protonation of [15]-54-219 annulenone below -45°C affords a mixture of [15]-54-90 and [15]-54-219 annulenyl ions.
- (ii) Thermal isomerization of [15]-54-219 annulenyl ion occurs at $-20\sim-30^{\circ}$ to give [15]-55-91 annulenyl ion. This process expells the inside OH group of the 54-219 conformer toward the outside of the ring.
- (iii) Deprotonation of [15]-55-91 annulenyl ion gives [15]-55-91 annulenone.
- (iv) Finally, [15]-54-219 annulenone is regenerated by the isomerization of [15]-55-91-annulenone.

Following observations were collected.

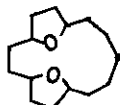
- (1) Isomerization of [15]-54-219 annulenyl ion is depressed by lowering temperature below -45°C .
- (2) Isomerization of [15]-54-219 annulenyl ion conducted at $-30\sim-20^{\circ}\text{C}$ afforded a mixture of possible isomers, such as [15]-55-88, and [15]-119-219 annulenyl ions.
- (3) Conformational change occurred in the second step of the cycle raises the $\text{p}k_{\text{a}}$ of [15]-55-91 annulenyl ion at least by ca. 1 than that of the 54-219-isomer.
- (4) [15]-55-91 annulenone was proved to be strongly diatropic.
- (5) Thermal isomerization of [15]-55-91 annulenone was studied kinetically in some detail by nmr spectroscopy.

Of course, we need much more intensive studies for the elucidation of this [15]annulenone-[15]annulenyl ion cycle.

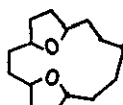
Cordification of all the possible isomers encounter in this cycle and related compounds was given as follows.



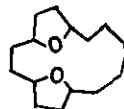
[15]-54-219



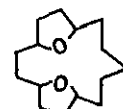
[15]-54-90



[15]-55-91



[15]-55-88



[15]-119-219