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On the Redox Properties of Cyclophosphanes

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On the Redox Properties of Cyclophosphanes

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While sulfur rings form stable, isolable dications, corresponding dications of cyclophosphanes are not known so far. Here we report on the electrochemical formation of the mono- and dication of I (R=N(i-propyl) $_2$). The monocation of I is a stable species, even at room temperature. On the contrary the corresponding dication rearranges under a sequence of fast 1.2-shifts of the substituents, even at temperatures below -80° C to intermediary 'carbene-like' structures, which finally fragment into the diamino-phosphenium cation, I, and I (which subsequently polymerizes). Quantum chemical investigations are in support of these findings and suggest a general model for the redox properties of cyclophosphanes.

$$R - P - R \qquad S = S$$

$$\frac{1}{R}$$

$$\frac{1}{R}$$

$$\frac{1}{R}$$

$$\frac{2}{R}$$

$$R = N = N$$

$$i-prop$$

$$i-prop$$

$$\frac{3}{R}$$