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Phosphorus, Sulfur, and Silicon and the Related Elements

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$^{31}\text{J}(\text{P},\text{C})$ Couplings in 3-Phosphabicyclo[3.1.0]Hexane 3-Oxides

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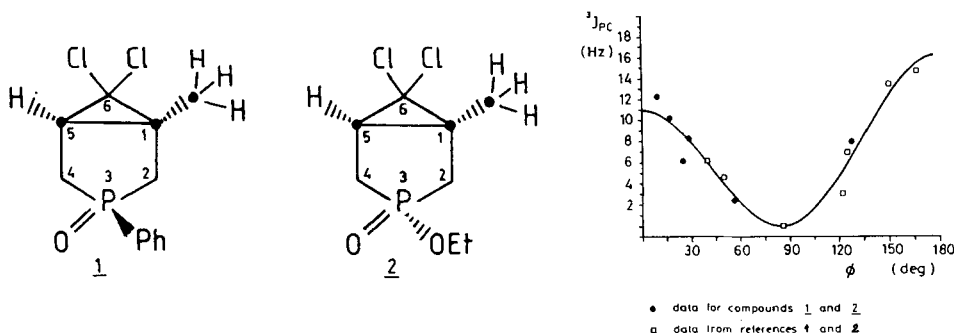
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$^3J(\text{P}, \text{C})$ COUPLINGS IN 3-PHOSPHABICYCLO[3.1.0]HEXANE 3-OXIDES

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Vicinal phosphorus-carbon couplings ($^3J(\text{P}, \text{C})$) measured for 3-phosphabicyclo[3.1.0]hexane 3-oxides (1 and 2) of known geometry have been studied. With one exception (see below), the dependence of the $^3J(\text{P}, \text{C})$ constants on the torsion angles (θ) followed the Karplus-equation ($^3J(\text{P}, \text{C}) = A \cos^2 \theta + B \cos \theta + C$).



On C_6 coupled through two vicinal paths by the phosphorus atom, extremely large constants (ca. 12 Hz) have been observed in 1 and 2 ($\theta \sim 77^\circ$). According to our explanation, "through space" coupling is responsible for the extraordinary large splitting.

The $176^\circ - 12.7 \text{ Hz}$ and $111^\circ - 0 \text{ Hz}$ data pairs obtained for 8-chloro-5,6-di(methoxycarbonyl)-4,7-dimethyl-2-ethoxy-2-phosphabicyclo-[2.2.2]octa-5,7-diene 2-oxide also fit the Karplus curve.

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