Double Intramolecular Process in Spirophosphoranes observed by Nuclear Magnetic Resonance Spectroscopy

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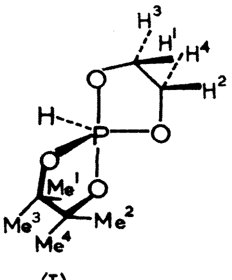
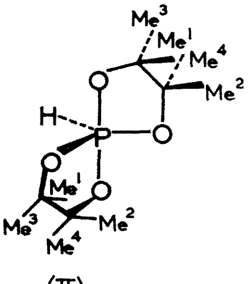
TEMPERATURE-DEPENDENT spectra have been observed for some penta-co-ordinated phosphorus compounds.[1] We report here some results concerning spirophosphoranes (I) and (II),[2] which also display temperature-dependent n.m.r. spectra.

The n.m.r. spectra of (I) and (II) recorded at 100 MHz. in perdeuteriotoluene with hexamethyldisiloxane as internal lock, at *ca.* 0°, exhibit a well separated doublet [808 Hz. for (I), 801 Hz. for (II)]; each component of the doublet corresponds to half a proton; and two sharp, separated methyl doublets for each compound: $\Delta\delta$Me 7·5 Hz. for (I); 10 Hz. for (II). The separation is due to a chemical shift, as proved by recording the spectra at 60 and 100 MHz.

For the compound (I), a complex AA′BB′X system is observed, corresponding to the methylene ring protons ${}^3J(\mathrm{PH_A}) = {}^3J(\mathrm{PH_{A'}}) = \pm\ 15{\cdot}5$ Hz., ${}^3J(\mathrm{PH_B}) = {}^3J(\mathrm{PH_{B'}}) = \pm\ 12$ Hz.). These two coupling constants are of the same sign.



(I)



(II)

As the temperature is raised, the two methyl peaks of (I) and (II) broaden, coalesce [T_c 37° for (I), 95° for (II)], and finally become a sharp line at high temperature. The AA′BB′X system of (I) changes into an A_4X system [${}^3J$(PH) 13·5 Hz.]. As the temperature is raised, the doublets corresponding to the proton directly bonded to the phosphorus atom remain unchanged. No change is observed in the spectra of (I) and (II) from 0° down to −70°.

Since ${}^1J$(PH) is independent of temperature and since in the high-temperature A_4X system of (I), ${}^3J$(PH) is the mean value of the ${}^3J$(PH) values obtained in the low-temperature AA′BB′X system, the observed exchange process is intramolecular. From structural data concerning penta-co-ordinated phosphorus compounds,[3] we assume that the phosphoranes (I) and (II) exist in a trigonal bipyramidal form, with the less electronegative substituent (H) in the equatorial plane[4] (see formulae). In the rigid forms, there must be four different kinds of protons in (I) (H^1, H^2, H^3, H^4) and four different kinds of methyls in (I) and (II) (symmetry (C_2) (Me^1, Me^2, Me^3, Me^4). Since in the low-temperature spectra there are only two sharp methyl signals in (I) and (II) (width at half height $w_{\frac{1}{2}}$ (I) 1·5 Hz., $w_{\frac{1}{2}}$ (II) 1·5 Hz.) and an AA′BB′X system for the ring protons of (I), an exchange process occurs at this temperature. The complete analysis of the AA′BB′X system of (I) indicates that $|J_{AB} + J_{AB'}| < |J_{AB} - J_{AB'}|$, so J_{AB} and $J_{AB'}$ are of opposite signs and J_{AB} is a geminal coupling constant (J_{AB} −8·7, $J_{AB'}$ +6·2 Hz). Consequently, the low-temperature exchange process makes equivalent the substituents which are *trans* with respect to the hydrogen directly bonded to the phosphorus on the one hand (H^1, H^2; Me^1, Me^2) and the substituents which are *cis* with respect to the hydrogen on the other hand (H^3, H^4; Me^3, Me^4). The high-temperature process renders equivalent all the substituents of one ring.

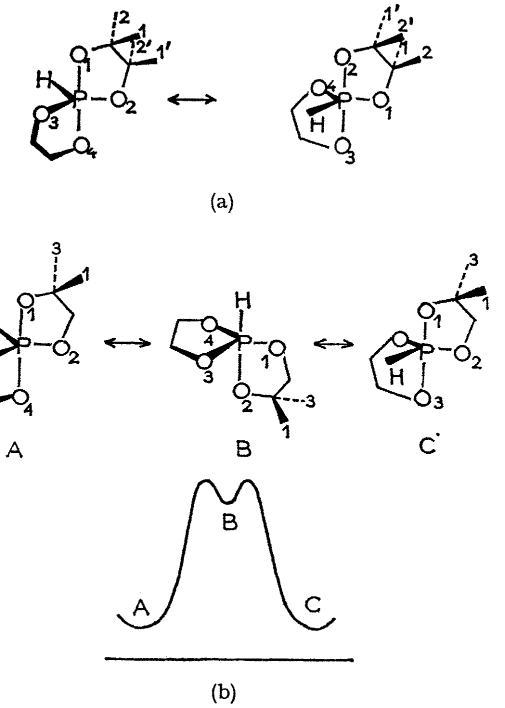


FIGURE (a) *Low-temperature process.*
(b) *Reaction co-ordinate. High-temperature process.*

These results can be explained by considering pseudorotation processes[5,6] (Figure b). From the observed spectral change, the mean lifetime τ in each stable state and the ΔG involved for the high-temperature process may be calculated. The existence of the transition state B with an hydrogen in the axial position introduces a transmission coefficient of $\frac{1}{2}$. The fact that one high-temperature process (A → C) renders the substituents of only one ring equivalent introduces another coefficient of $\frac{1}{2}$.

$$\text{Thus } \tau(\mathrm{I}) = 3{\cdot}0 \times 10^{-2}\ \text{sec.} \quad \Delta G(\mathrm{I}) = 15{\cdot}6\ (\text{kcal./mole})$$

$$\tau(\mathrm{II}) = 2{\cdot}2 \times 10^{-2}\ \text{sec.} \quad \Delta G(\mathrm{II}) = 18{\cdot}4\ (\text{kcal./mole})$$

(*Received, February 17th,* 1969; *Com.* 211.)

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