Synthesis of Tetrafluoro(pentane-2,4-dionato)phosphorus(V) and Analogous Compounds

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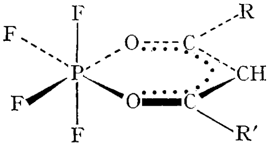
WE report the synthesis of a new chelate system containing sp^3d^2-hybridised phosphorus.

A dry ethereal solution of acetylacetone was saturated with phosphorus pentafluoride at −70° and allowed to warm to room temperature. The residue, after removal of the solvent and excess of phosphorus pentafluoride *in vacuo*, was crystallised from chloroform–ether to give tetrafluoro(pentane-2,4-dionato)phosphorus(v) (I, R=R′=Me) as stable white crystals m.p. 85° (50% yield).



(I)

The elemental analyses and spectroscopic properties (see below) are consistent with this structure, in which phosphorus in an octahedral environment, attains its covalence maximum of six. The structure is analogous to that of the tetrahedral difluoroboron chelates[1] formed from β-diketones and boron trifluoride in which boron attains its normal covalence maximum of four.

The i.r. spectrum (KBr disc) showed no bands in the normal carbonyl region, but had strong bands at 1560 (C⩶C str.) and 1425 cm.$^{-1}$ (C⩶O str.) characteristic of the chelated β-diketone moiety,[2] while six strong peaks in a complex band between 890 and 790 cm.$^{-1}$ are ascribed to coupled modes of P–F and P–O stretching vibrations.[3] The u.v. spectrum λ_{max} ($CHCl_3$) 290 mμ; ϵ, 14,900, when compared with that of the enol form of acetylacetone, has the bathochromic shift and increased intensity associated with $\pi \rightarrow \pi^*$ transitions in covalently bonded β-diketone chelates.[4] The proton and fluorine n.m.r. spectra were obtained in deuterochloroform at 33·5° at 40·004 and 37·644 Mc./sec. respectively. The proton spectrum showed two signals at τ 7·68 and 3·86 of relative intensity 6 and 1. The former, ascribed to the two equivalent methyl groups, was a doublet due to coupling to the phosphorus atom, $J(P\text{–}CH_3)$ 2c./sec., the latter was a broadened single line, showing evidence of a smaller coupling to the phosphorus atom, and is ascribed to the 3-hydrogen atom. Both signals are significantly moved to lower field compared with the corresponding signals of the enol form of acetylacetone. The shifts are comparable with these observed in diamagnetic metal acetylacetonates,[5] in the cationic tris-(acetylacetonato)silicon,[6] and in the corresponding difluoroboron chelates.[1,7] They are considerably larger than the shifts found in the diakylboron complexes of acetylacetone[8] and in the dihalogenotin complexes of β-diketones.[9] The fluorine spectrum shows 28 lines, corresponding to the 14 lines of an A_2B_2 system,[10] each line being doubled by coupling to the phosphorus atom. Analysis of the spectrum gave the following parameters[11]: ϕ^*_{axial} + 53·87, $\phi^*_{equatorial}$ + 73·81; $J_{PF\,axial}$ ± 824, $J_{PF\,equatorial}$ ± 741, J_{ae} 59·4 c./sec. (*cf.* ref. 12).

Analogous compounds (I, R=Me, R′=Ph; I, R=R′=Ph) with similar properties were formed when benzoylacetone and dibenzoylmethane were similarly treated with phosphorus pentafluoride, and the reaction is being extended to other β-diketones.

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