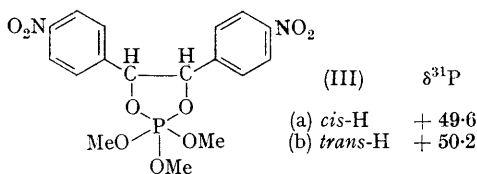
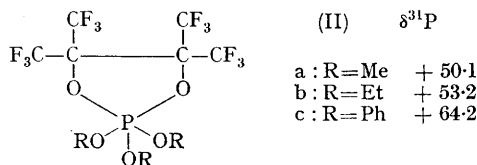
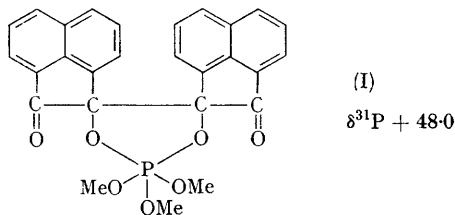


# Pentaoxyphosphoranes from the Reaction of Fluorenone with Trialkyl Phosphites

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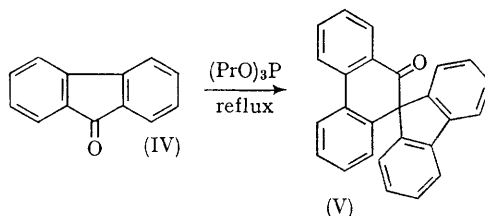
THE first observable product of the reaction of trialkyl phosphites with acenaphthenequinone was the 1,3,2-dioxaphospholan (I).<sup>1</sup> Similar types of products, (II) and (III), were obtained from the reaction of trialkyl phosphites with hexafluoroacetone<sup>2</sup> and with *p*-nitrobenzaldehyde.<sup>3</sup>



Such results<sup>1</sup> show that trialkyl phosphites tend to add to the oxygen of carbonyl functions which are activated by electron-withdrawing groups. Benzaldehyde, acetone, and benzophenone do not react with trialkyl phosphites at 20°, but, at *ca.* 170° reaction has been observed between trialkyl phosphites and certain aromatic ketones.<sup>4</sup> Thus, fluorenone with boiling tri-isopropyl phosphite was said to give the spiro-compound (V), and tri-isopropyl phosphate. No intermediates were detected.

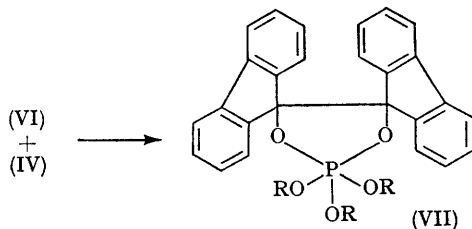
Trialkyl phosphites added slowly, but cleanly, to the oxygen of fluorenone (IV), at 20° in methylene chloride solution. The 1:1 adduct (VI) had a negative charge forming part of a cyclopentadienide system, and was thus relatively stable.<sup>5</sup> However, as with hexafluoroacetone and related compounds,<sup>2,3</sup> the adduct reacted rapidly with

more fluorenone to form a 2:1 adduct, a 2,2,2-trialkoxy-1,3,2-dioxaphospholan (VII).



The order of reactivity of the trialkyl phosphites toward fluorenone was  $(\text{Pr}^i\text{O})_3\text{P} > (\text{EtO})_3\text{P} > (\text{MeO})_3\text{P}$  (reaction was nearly complete in 3, 7, and 20 days, respectively when 5M-solutions of the reagents in methylene chloride were stirred at 20°). The m.p.s and yields of products are listed in the Table. The phospholane gave satisfactory elemental analyses. The quinquecovalency of the phosphorus in the 2:1 adducts was based on comparison of <sup>31</sup>P n.m.r. shifts with those of related compounds.<sup>1,6</sup>

The phospholans varied greatly in thermal stability. The fluorenone-tri-isopropyl phosphite adduct (VIIc), decomposed into the spiro-compound (V), and tri-isopropyl phosphate in boiling benzene. The corresponding adducts from triethyl phosphite and trimethyl phosphite were stable under comparable conditions. At 161° (diglyme) all of the adducts decomposed to the corresponding phosphates and (V); fluorenone was also produced.



Evidently, the dioxaphospholans underwent two types of processes when heated; dissociation to fluorenone and the phosphite, and a pinacolic rearrangement shown schematically by (VIII)  $\rightarrow$  (IX) (IX  $\equiv$  V). Related rearrangements of other

TABLE

| (VII) | R                          | % yield | m.p.   | $\delta^{31}\text{P}^a$ | $\tau(\text{H}_\alpha)^b$ | $J(\text{PH}_\alpha)$ | $\tau(\text{H}_\beta)^b$ | $J(\text{PH}_\beta)$ |
|-------|----------------------------|---------|--------|-------------------------|---------------------------|-----------------------|--------------------------|----------------------|
| a     | $\text{CH}_3$              | 60      | 162-4° | +46.7                   | 6.26                      | 13.5                  | —                        | —                    |
| b     | $\text{CH}_2\text{CH}_3$   | 70      | 143-5° | +49.3                   | 5.85                      | 7.1 <sup>c</sup>      | 8.72                     | 1.8                  |
| c     | $\text{CH}(\text{CH}_3)_2$ | 70      | 146-8° | +52.2                   | 5.20                      | 7.0 <sup>d</sup>      | 8.66                     | 0.8                  |

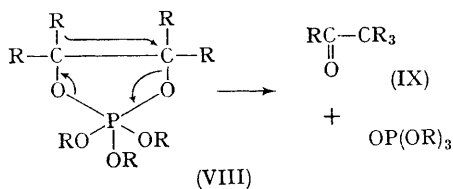
<sup>a</sup> relative to 85%  $\text{H}_3\text{PO}_4$  as zero in  $\text{CDCl}_3$  solution at 40.5 Mc./sec.

<sup>b</sup> in  $\text{CDCl}_3$  at 60 Mc./sec.  $\text{P}-\text{O}-\text{CH}_\alpha-\text{CH}_\beta$

<sup>c</sup> a doublet of quartets with  $J(\text{H}_\alpha\text{H}_\beta) \approx J(\text{PH}_\alpha)$

<sup>d</sup> a doublet of septets with  $J(\text{H}_\alpha\text{H}_\beta) \approx J(\text{PH}_\alpha)$

pentaoxyphosphoranes [have already been reported].<sup>1,7</sup>



These results elucidate the nature of the processes that generated the pinacolone type of product (V) in the reaction of fluorenone with boiling tri-isopropyl phosphite reported by Poshkus.<sup>4</sup> It was verified that (V) was one of the

products of the pyrolysis of the fluorenone-triethyl phosphite adduct carried out in boiling triethyl phosphite as solvent; in addition, considerable fluorenone was also produced. In other words, the phosphite ester is in no way involved in the formation of (V).

The reactions of aromatic monoketones with trialkyl phosphites at elevated temperatures are mechanistically different from the reductive dimerization of phthalic anhydride to biphthalyl by trialkyl phosphites.<sup>8</sup> The only common feature of these two types of reactions is the initial formation of a 1:1 adduct having a P-O-C bond.<sup>1</sup>

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