Alkaline Hydrolysis of 2,2,3,4,4-Pentamethyl-1-phenylphosphetanium Bromide

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WE have reported[1] that treatment of the phosphetanium bromide (Ia)† with cold, dilute sodium hydroxide produced the hexahydrophosphanaphthalene (IIa).‡ Trippett and his co-workers in an independent study[2] have assigned structure (IIIa) to this product.

Structure (IIa) is supported by (*a*) conversion into (IV), m.p. 157—159°, with 30% Pd-C in

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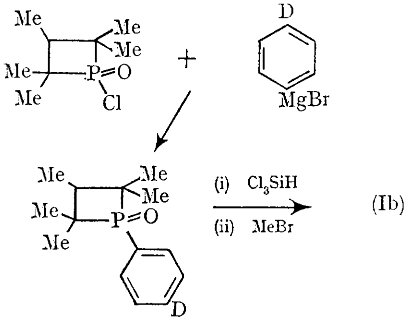
† The iodide can also be used.

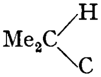
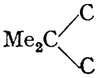
‡ The m.p. of the oxide is variable owing to its hygroscopic property. A freshly sublimed sample has m.p. 149—159° (open capillary) but 163—165° in a sealed, evacuated capillary. Samples which have stood in the open, melt at lower temperatures than those above.

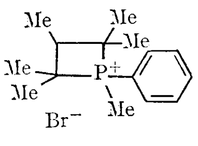
refluxing decalin; (*b*) the ^{1}H n.m.r. and associated ^{31}P–^{1}H decoupled spectra. However, the absence of u.v. absorption for a cyclohexa-1,3-dienyl chromophore is inconsistent with (IIa) but is accommodated by (IIIa). On the other hand the broad doublet (τ 7·02—7·49, the centres of which are *ca.* 16 c./sec. apart) due to the allyl protons collapsed to a broad singlet on ^{31}P–^{1}H decoupling. The allyl protons in (IIIa) are five bonds away from phosphorus; analogous systems[3] (γ-methylallylphosphorus derivatives) show $^{5}J_{PH}$ 4—5·8 c./sec.

In order to establish unambiguously the structure for the rearrangement product, a definitive labelling experiment was performed; (Ib) was prepared[4] by the sequence:

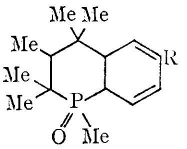


Hydrolysis (NaOH–H_2O) of (Ib) gave a compound whose n.m.r. spectrum was in accord with (IIIb) (vinyl:allyl proton ratio of 4:1); similar treatment of (Ib) with NaOD–D_2O produced (IIIc). The labelling study excludes (IIb) and the isomeric 1,3-diene of (IIIb).

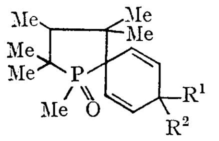
The formulation for the aromatic compound (IV) remains unchanged; the n.m.r.,[1] and i.r. spectra, and combustion analysis are in agreement with this structure. The alternative possibilities PhCMe$_2$·CHMe·CMe$_2$·P(O)HMe and PhMeP(O)·CMe$_2$·CHMeCHMe$_2$ are untenable structures. The former material, m.p. 126—129°, was prepared from (IIIa) *via* a Hoffmann-type elimination and shows P–H stretching (ν_{max} 2290 cm.$^{-1}$) in the i.r. spectrum. The n.m.r. spectrum of the latter compound would give a doublet due to the  $\mathrm{Me_2C}{<}^{\mathrm{H}}_{\mathrm{C}}$ group; however, a singlet corresponding to  $\mathrm{Me_2C}{<}^{\mathrm{C}}_{\mathrm{C}}$ was observed.



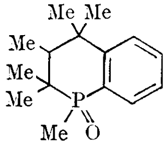
(Ia) R=H
(Ib) R=D



(IIa) R=H
(IIb) R=D



(IIIa) R^1=R^2=H
(IIIb) R^1=H,R^2=D
(IIIc) R^1=R^2=D



(IV)

The generality and mechanisms of (I) → (II) → (III) are under investigation.

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[1] S. E. Cremer and R. J. Chorvat, Abstracts 154th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1967, S047; S. E. Cremer and R. J. Chorvat, *Tetrahedron Letters*, 1968, 413.

[2] S. Trippett, W. Hawes, S. E. Fishwick, and J. Flint, *Chem. Comm.*, 1967, 1113.

[3] M. Gordon and C. E. Griffin, *J. Org. Chem.*, 1966, **31**, 333; M. Gordon, Ph.D. Thesis, University of Pittsburgh, 1965.

[4] S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 1967, **32**, 4066. Either phenyl-lithium or the Grignard may be used in the first step of this sequence.