The Reactions of Phosphetans with Halogens. A New Phospholene Synthesis

By J. R. CORFIELD, M. J. P. HARGER, R. K. ORAM, D. J. H. SMITH, and S. TRIPPETT*

(*Department of Chemistry, University of Leicester, Leicester,* LE1 7RH)

Summary 2,2-Dimethylphosphetans with chlorine or bromine give but-3-enylhalogenophosphines which cyclise to phospholenes on heating or on treatment with halogen and to phospholenes and/or phosphetan oxides with aluminium chloride.

TREATMENT of the phosphetans (1; R = Cl, Ph) and (2) with one mole of chlorine in 1,2-dichloroethane at -20° followed by distillation gave the acyclic chlorophosphines (3; R = Cl, Ph) and (4), *e.g.* (4) (61%), b.p. 89°/0·05 mm, τ 8·85 (s, 6H), 8·4 (s, 3H), 7·64 (s!, 2H), 5·2 (m, 2H), and

1·9—2·7 (m, 5H) and (3; R = Ph) (93%), b.p. 124°/0·6 mm as a mixture of diastereoisomers. At 150° or on treatment with chlorine these *P*-phenyl chlorophosphines cyclised almost quantitatively to the corresponding phospholenes, the 2-phospholene (5) b.p. 140—142°/1 mm, τ 8·98 (s, 3H), 8·83 (s, 3H), 8·11 (s, 3H), 7·4—8·2 (m, 2H), 4·25 (d, 1H, J_{PH} 37 Hz), and 2·1—2·9 (m, 5H), from (4); and the 3-phospholene (6), containing 3% of the 2-phospholene, from (3; R = Ph). Hydrogen chloride did not catalyse these cyclisations.

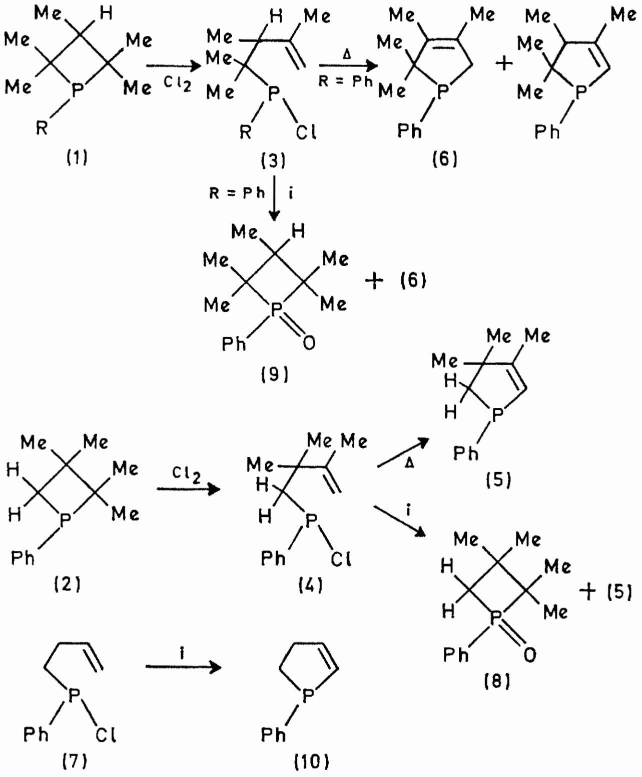
The phosphetans (1; R = Ph) and (2) with bromine in methylene chloride at −20° followed by distillation gave the phospholene hydrobromides, that of (6) (77%) b.p. 108°/0·6 mm, containing 18% of the hydrobromide of the 2-phospholene; and that of (5) (84%), b.p. 109°/0·4 mm, respectively. These hydrobromides showed ν_{max} 2440 and 2200—2300 cm^{-1} and a very broad P–H doublet at τ 0·5 (J_{PH} *ca.* 530 Hz). Treatment with 1 equiv. of alkali gave the phospholenes, which with hydrogen bromide in benzene re-formed the hydrobromides. No signal could be detected in the ^{31}P n.m.r. spectra of these hydrobromides. The intermediate acyclic bromophosphines could not be isolated.

The cyclisation of alk-3-enylhalogenophosphines to give phospholenes is aided by a 3-methyl substituent. Thus but-3-enylchlorophenylphosphine (7) did not cyclise at 190° or on treatment with chlorine or bromine.

Aluminium chloride-catalysed cyclisation of alk-3-enylchlorophosphines followed by treatment with water led to phosphetan oxides and/or phospholenes, the former being favoured by a 3-methyl substituent. Thus while (4) gave the phosphetan oxide (8) (38%) and the 2-phospholene (5) isolated as the oxide (30%), and (3) gave the isomeric phosphetan oxides (9) (37% of 1 : 1-*cis* : *trans*) together with a mixture of 2- and 3-phospholenes (36% of 1 : 5), the but-3-enylchlorophosphine (7) gave only the 2-phospholene (10) isolated as the oxide (60%).

Formation of the four- and of the five-membered rings in these reactions presumably involves co-ordination of the aluminium chloride to the olefin and to the phosphorus, respectively.

The above reactions allow the synthesis from readily available phosphetans of phospholenes having a wider range of substituents than hitherto available.[1]



Reagent: (i) $AlCl_3$–$(ClCH_2)_2$; H_2O.

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[1] K. D. Berlin and D. M. Hellwege, *Topics Phosphorus Chem.*, 1969, **6**, 1.