A Stable Four-membered-ring Ylid–Ketone Adduct

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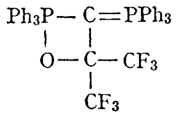
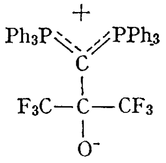
IN the Wittig reaction it is usually assumed that the formation of phosphine oxide and olefinic products from phosphorane and carbonyl reactants proceeds by way of a betaine which cleaves *via* a cyclic transition state.[1–3] In some cases stabilized betaine intermediates have been isolated.[2–4] A stable adduct that we have synthesized from hexafluoroacetone and hexaphenylcarbodiphosphorane, however, appears to have the unusual covalent cyclic structure (Ia) rather than the expected betaine structure (Ib).



(Ia)



(Ib)

In a typical reaction, gaseous hexafluoroacetone was dispersed in a stirred mixture of hexaphenylcarbodiphosphorane (II)[5,6] (21·4 g., 0·04 mole) and dry Diglyme (65 g.) under nitrogen at 40—50°. The flow of hexafluoroacetone was continued for ½ hr. after the yellow colour of (II) disappeared. The reaction mixture was then cooled at 5° for 3 hr. and filtered under nitrogen. The resulting product was washed with Diglyme and diethyl ether to give a white solid (21·5 g., 76% yield), m.p. 155—157° (decomp.; 157—158° from Diglyme–diethyl ether); molecular weight by osmometry in benzene, 706 and 700 (theoretical for a 1 : 1 adduct, 702·6).* N.m.r. measurements indicate that this adduct is 4,4-bis(trifluoromethyl)-2,2,2-triphenyl-3-(triphenylphosphoranylidene)-1,2-oxaphosphetane (Ia) rather than the phosphobetaine (Ib). The ^{31}P n.m.r, spectrum exhibited doublets of equal area at $-7{\cdot}3 \pm 0{\cdot}2$ p.p.m. and at $+54{\cdot}0 \pm 1{\cdot}0$ p.p.m., $J_{PP'} = 47 \pm 7$ c./sec. (relative to H_3PO_4 and measured in a saturated methylene chloride solution at both 24·3 and 40·5 Mc./sec.). Two doublets would be expected from spin-coupling of the two non-equivalent phosphorus atoms of (Ia), the doublet at $-7{\cdot}3$ p.p.m. being within the phosphorus ylid range and the doublet at $+54{\cdot}0$ p.p.m. being characteristic of cyclic structures having phosphorus covalently bonded to five substituents.[7] The two equivalent phosphorus atoms of the mesomeric phosphonium structure (Ib) would be expected to exhibit only a single ^{31}P resonance at about -20 p.p.m.[8] The ^{19}F spectrum contained a poorly resolved doublet at $+71{\cdot}2 \pm 0{\cdot}2$ p.p.m. (relative to CCl_3F), the slight splitting (~0·8 c./sec.) probably resulting from preferential spin-coupling of the six equivalent fluorine atoms with one of the phosphorus atoms of (Ia). The ^1H spectrum had a multi-peak aryl hydrogen region at $-6{\cdot}5$ to $-8{\cdot}0$ p.p.m. (relative to tetramethylsilane), a comparatively broad absorption which is consistent with the unsymmetrical structure of (Ia) but not with (Ib) in which all of the phenyl groups have equivalent environments.

The adduct was not alkylated when stirred in an excess of methyl iodide or when warmed at 40—45° for 20 hr. in a methanol solution containing methyl iodide. This stands in contrast to the ready alkylations by methyl iodide which occurred with the adducts of (II) and carbon dioxide or carbon disulphide,[9] and with Wittig and Haag's stable adduct obtained from isopropylidenetriphenylphosphorane and diphenylketen,[4] and provides further evidence that the compound does not have the ionic structure (Ib).

Acid treatment of (Ia) results in narrowing of the ^1H n.m.r. absorption to about 1 p.p.m. and replacement of the two ^{31}P doublets by a moderately broad singlet at about -22 p.p.m. This is consistent with ring-opening of (Ia) and formation of symmetrical mesomeric phosphonium salts (III). For example, the treatment of a Diglyme solution of (Ia) with hexafluorophosphoric acid gave an 83% yield of white solid (III; $X = PF_6$), m.p. 213—213·5° (decomp.). The ^{31}P n.m.r. spectrum of an acetonitrile solution of this salt showed a moderately broad signal at $-21{\cdot}6$ p.p.m. for the two equivalent phosphorus atoms of the cation and contained a heptet at $+144{\cdot}8$ p.p.m. ($J_{PF} = 706$ c./sec.) for the hexafluorophosphate anion; the ^1H spectrum consisted of a comparatively simple aryl hydrogen region at $-7{\cdot}1$ to $-8{\cdot}0$ p.p.m. and a broad hydroxylic hydrogen absorption at $-6{\cdot}3$ p.p.m., the areas approximating the theoretical 30 : 1 ratio; and the ^{19}F spectrum contained a singlet at $+71{\cdot}6$ p.p.m. for the fluorine atoms of the cation and a doublet at $+72{\cdot}5$ p.p.m. ($J_{FP} = 709$ c./sec.)

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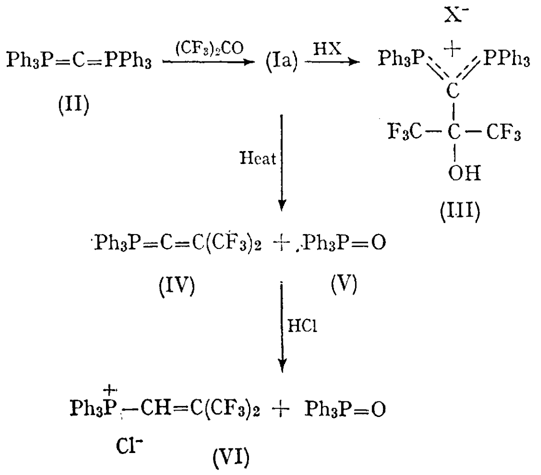
* Satisfactory elemental analyses were obtained for all new compounds that were isolated.

for the anion, the area ratio of singlet to doublet being 1 : 1.



The Wittig reaction sequence was completed by warming (Ia) above 110° in inert solvents. A new vinylidenephosphorane (IV) was obtained which proved to be too reactive for ready separation from the accompanying triphenylphosphine oxide (V) by-product. The ^{31}P n.m.r. spectrum of the resulting orange mixture in benzene consisted of a singlet at $-24\cdot5 \pm 0\cdot5$ p.p.m. for (V) and a singlet at $-4\cdot1 \pm 0\cdot2$ p.p.m., the latter singlet and an ^{19}F doublet at $+61\cdot4 \pm 0\cdot4$ p.p.m. ($J_{FP} = 3\cdot5$ c./sec.) being attributed to (IV).

Addition of anhydrous hydrogen chloride to a benzene solution of the mixture of (IV) and (V) resulted in precipitation of the hydrogen chloride adduct (VI), a light yellow solid, m.p. 153—154° (decomp.). The ^{31}P n.m.r. spectrum of (VI) in $CDCl_3$ had a singlet at $-17\cdot3 \pm 0\cdot2$ p.p.m.; the ^1H spectrum had a doublet at $-9\cdot1$ p.p.m. ($J_{HP} = 8\cdot5$ c./sec.) and aryl hydrogen multiplets at $-7\cdot5$ to $-8\cdot3$ p.p.m., the areas approximating a 1 : 15 ratio; and the ^{19}F spectrum had quarters of equal area at $+58\cdot1$ and $+62\cdot3$ p.p.m. ($J_{FF'} = 7\cdot5$ c./sec.). Triphenylphosphine oxide was isolated from the filtrate.

(*Received, January 2nd,* 1967; *Com.* 008.)

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