**Tetrahedron Letters No.25, pp. 2833-2836, 1966. Pergamon Press Ltd.
Printed in Great Britain.**

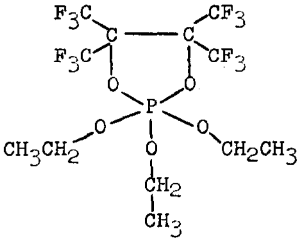
THE REACTION OF HEXAFLUOROACETONE AND TRIPHENYLPHOSPHINE
[2,2-DIHYDRO-2,2,2-TRIPHENYL-4,4,5,5-TETRAKIS(TRIFLUOROMETHYL)-1,3,2-DIOXAPHOSPHOLANE]

By

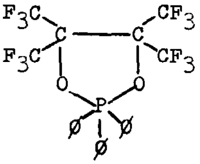
Richard F. Stockel
Research and Development
Organic Chemicals Division
American Cyanamid Company
Bound Brook, New Jersey

(Received 23 February 1966; in revised form 6 April 1966)

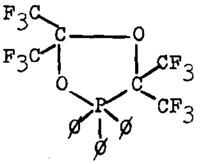
Two recent communications[1,2] describe the reaction of triethylphosphite and hexafluoroacetone. The adduct formed is a phospholane with the structure (I). Nonfluorinated phospholanes and phospholenes have been previously reported and critically investigated by Ramirez and co-workers[3].



(I)



(II)



(III)

Interestingly, a phospholane (II) is found when triphenylphosphine is used. This is the first case reported for a 1,3,2-dioxaphospholane with phosphorus bonded to three carbon atoms. The adduct decomposes at 105-106°C. The crystals are colorless monoclinic tablets. It is prepared by adding an equivalent amount of triphenylphosphine dissolved in ethyl ether to hexafluoroacetone at -28°C. The phospholane is formed in quantitative yield with a very high degree of purity. It can be recrystallized from methanol-water.

Structure assignment is based on the following evidence: analysis calculated for $C_{24}H_{15}F_{12}O_2P$: C, 48.50; H, 2.57; P, 5.21. Found: C, 48.15; H, 2.47; P, 5.23. Molecular weight (vapor pressure) theory 594; found 575. An alternate structure (III) was ruled out by infrared and F^{19} n.m.r. H^1 n.m.r. and P^{31} n.m.r. are also in agreement with structure (II).

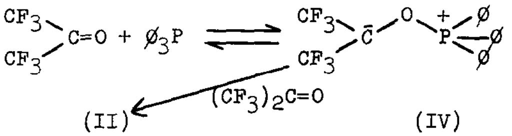
The infrared spectrum clearly shows the C-F group with several bands in the 1200 cm.$^{-1}$ region and one band at 1330 cm.$^{-1}$. The ϕ_3P moiety absorbs at 1095 cm.$^{-1}$, while the phenyl group absorbs at 3050, 1585, 1480, 1430, 990 and several bands between 750-690 cm.$^{-1}$. The choice of structure (II) over (III) is supported by a lack of a band at 1050 cm.$^{-1}$ which would be indicative of a O-C-O group. This latter evidence is not unequivocal.

The F^{19} n.m.r.[4b] run in $CH_3OH(CFCl_3)$ shows only one single peak at +65.2ϕ. This equivalence of fluorine strongly favors structure (II). If the adduct had been structure (III), then the F^{19} n.m.r. would have given rise to two singlets due to the different chemical environment of the two hexafluoroisopropylidene groups.

The H^1 n.m.r.[4a] run in C_6D_6 $\angle(CH_3)_4Si\underline{7}$ shows two absorptions in the aromatic region at 7.05 and 7.75 δ. The proton ratios are 3:2, accounting for the phenyl being attached to the phosphorus.

The P^{31} n.m.r.[4c] run in DMF $\angle(CH_3CH_2)_3PO_4\underline{7}$ shows only one peak at +18.6 p.p.m. This value is in the right range using the P^{31} n.m.r. data compiled by Professor Ramirez[3,5].

A plausible mechanism for the formation of these phospholanes involves a 1,3-dipolar system (IV)[3]. Attempts to trap this species with bicycloheptadiene and acetylenedicarboxylate have failed. This could mean that the dipolar species is more reactive with hexafluoroacetone than it is with the trapping olefins. This type of 1,3-dipolar addition appears to be without precedent at the present time[6].



An alternate mechanism would involve a concerted path as proposed for hexafluoroacetone and triethylphosphite[1]. This seems unlikely because it would involve the polarization of one carbonyl group to be in one direction $\overset{+\!\longrightarrow}{C{=}O}$ while in the second molecule the carbonyl would be polarized in the opposite direction $\overset{\longleftarrow\!+}{C{=}O}$. Besides, the kinetics would be termolecular which is a rare occurrence.

The chemistry of (II) is analogous to that of (I)[1,2] and appears to be straightforward. Hydrolysis of (II) gives a 65% yield of dodecafluoropinacol isolated as the dioxane adduct and triphenylphosphine oxide. Vigorous heat treatment at 180-200°C. gave triphenylphosphine oxide in the residue and hexafluoroacetone and other unidentified products in the distillate.

Finally, the reaction of hexafluoroacetone and triphenylarsine under these conditions failed to yield any product. This is no doubt due to the reduced nucleophilicity of triphenylarsine compared to triphenylphosphine.

Acknowledgments

The author greatly appreciates the helpful assistance of Dr. J. J. Lancaster for the n.m.r. spectra and Professor F. Ramirez for useful discussions on this subject.

References

1. N. P. Gambaryan, Yu. A. Cherburkov and I. L. Knunyants, Bull. Acad. Sci. U.S.S.R., 8, 1433 (1964).
2. E. M. Rokhlin, Yu. V. Zeifman, Yu. A. Cheburkov, N. P. Gambaryan, and I. L. Knunyants, D. O. Klady Akad. Nauk U.S.S.R., 161, 1356 (1965).
3. For an excellent review on this subject, see F. Ramirez, Pure Appl. Chem., 9, 337 (1964).
4. (a) Varian A-60 operating at 60 Mc, (b) Varian HR-60 operating at 56.4 Mc, (c) Varian DP-60 operating at 16.2 Mc.
5. In a private communication Professor Ramirez disclosed that similar reactions were being conducted in his laboratories using P^{31} n.m.r. data as a means of identifying the type of product formed. E.g., see F. Ramirez, O. P. Madan and C. P. Smith, J. Amer. Chem. Soc., 86, 5339 (1964).
6. R. Huisgen, Angew. Chem. Internat Ed. 2, 568 (1963).