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Alcohol to Ester Rearrangement. II. Diphenylphosphine and Hexafluoroacetone

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The reaction of diphenylphosphine with hexafluoroacetone gives $(C_6H_5)_2PC(OH)(CF_3)_2$ which is readily oxidized to $(C_6H_5)_2P(O)C(OH)(CF_3)_2$ and, in the presence of base catalyst, undergoes rearrangement to the isomeric $(C_6H_5)_2P(O)OCH(CF_3)_2$. Reaction of hexafluoroacetone with diphenylarsine gives $(C_6H_5)_2AsC(OH)(CF_3)_2$ while reaction with diphenyl phosphonate gives $(C_6H_5O)_2P(O)C(OH)(CF_3)_2$ which rearranges to $(C_6H_5O)_2P(O)OCH(CF_3)_2$.

La réaction de la diphénylphosphine sur l'hexafluoroacétone conduit à $(C_6H_5)_2PC(OH)(CF_3)_2$ qui s'oxyde facilement en $(C_6H_5)_2P(O)C(OH)(CF_3)_2$, ce dernier s'isomérise en $(C_6H_5)_2P(O)OCH(CF_3)_2$ selon un réarrangement catalysé par une base. La réaction de l'hexafluoroacétone sur la diphénylarsine conduit à $(C_6H_5)_2AsC(OH)(CF_3)_2$ et sur la diphénylphosphonate fournit $(C_6H_5O)_2P(O)C(OH)(CF_3)_2$ qui se réarrange en $(C_6H_5O)_2P(O)OCH(CF_3)_2$. [Traduit par le journal]

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Recently we reported the kinetics and mechanism of the base-catalyzed rearrangement of phosphorus(V) alcohols to the isomeric esters (eq. 1) (1). The alcohols were readily prepared

[1]
$$\begin{array}{ccc} OOH & O H \\ \parallel \parallel \\ (RO)_2 PC(CF_3)_2 & \xrightarrow{\text{Base}} & (RO)_2 POC(CF_3)_2 \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

by the reaction of dialkyl phosphonates with hexafluoroacetone. Whether phosphorus(III) alcohols would behave similarly is of some interest in view of the report that reaction of diphenylphosphine and hexafluoroacetone gives a 1:1 adduct involving trivalent carbon (2). The reaction of hexafluoroacetone with diphenylphosphine was therefore repeated, as well as reaction with diphenylphosphine oxide, diphenyl phosphonate, and diphenylarsine.

Our results from the reaction of diphenylphosphine and hexafluoroacetone are entirely consistent with the initial formation of a phosphorus(III) alcohol of structure **1** (eq. 2).

[2]
$$(C_6H_5)_2PH + (CF_3)_2CO \longrightarrow (C_6H_5)_2PC(CF_3)_2$$

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Compound 1 is a white solid, soluble in tetrahydrofuran (THF) and very susceptible to oxidation. Oxidation prevented satisfactory elemental analysis; however, the oxidized product 2 is stable in air and gave satisfactory elemental analysis. Rearrangement of alcohol 2 to ester 3 occurred in the presence of a base catalyst such as THF or pyridine, consistent with the alcohol to ester rearrangement described previously (1).

The ¹⁹F n.m.r. spectra were particularly useful in characterizing compounds 1, 2, and 3 and monitoring the rearrangement of 2 to 3. Figure la shows a typical ¹⁹F n.m.r. spectrum of a mixture of 1, 2, and 3 in THF in a sealed n.m.r. tube. The spectrum shown in Fig. lb was recorded 5 h after that shown in Fig. la and it is evident that concentration of 2 has decreased whereas 3 increased, confirming the alcohol-toester rearrangement in THF (eq. 3). The rate of rearrangement may be increased by introducing a stronger base such as pyridine. During the rearrangement, the concentration of 1 remained unchanged, confirming that 1 is stable in THF provided that oxygen and moisture are excluded.

An alternate route to 3, involving rearrangement of 1 to $(C_6H_5)_2$ POCH $(CF_3)_2$ followed by oxidation to 3 was not observed in our study.

In a separate experiment it was shown that reaction of diphenylphosphine oxide with hexafluoroacetone gave 2 and addition of pyridine catalyzed the rearrangement to 3. Similarly, reaction of diphenyl phosphonate with hexafluoroacetone gave alcohol 4 and addition of pyridine gave the isomeric ester 5 (eq. 4).

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FIG. 1 (a) The 19 F n.m.r. spectrum of mixture of 1, 2, and 3 in tetrahydrofuran. (b) After 5 h at 25°. Concentration of 2 decreased, 3 increased while 1 remained unchanged.

$$[4] (C_6H_5O)_2P(O)H + (CF_3)_2CO \longrightarrow$$

$$\begin{array}{ccc} & & & & O & H \\ \parallel \parallel & & & \\ (C_6H_5O)_2PC(CF_3)_2 & \xrightarrow{Base} & (C_6H_5O)_2POC(CF_3)_2 \\ & & & & \\ & & & & 5 \end{array}$$

The reaction of diphenylarsine with hexafluoroacetone was carried out in an attempt to prepare a stable arsenic(III) alcohol analogous to 1 (eq. 5). Reaction occurred readily to give 6, OH

$$[5] (C_6H_5)_2A_5H + (CF_3)_2CO \longrightarrow (C_6H_5)_2A_5C(CF_3)_2$$

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an oily liquid which was more resistant to oxidation than 1 and gave satisfactory elemental analysis. The reaction of dimethylarsine with hexafluoroacetone to give an arsenic(III) alcohol has been reported by Cullen and Styan (4). Oxidation of $\mathbf{6}$ with gaseous oxygen gave bis (diphenylarsine) oxide.

Recent investigations have shown that phosphorus(III) derivatives may abstract fluorine attached to a carbon atom (5). During this study it was observed that if 1 was left in the presence of excess hexafluoroacetone, fluorine abstraction

$$[6] \qquad 1 \xrightarrow{(CF_3)_2CO \text{ excess}}_{\text{or } XeF_2} \xrightarrow{(C_6H_5)_2PC(CF_3)_2}_{F}$$

occurred to give 7 (eq. 6). Addition of a fluorinating agent such as XeF_2 (6) to 1 also gave 7, which was identified on the basis of its ¹⁹F n.m.r. and mass spectra. The ease of fluorination and oxidation is consistent with the structure proposed for 1.

Experimental

Conventional vacuum line techniques were used for handling volatile materials. Hexafluoroacetone (Matheson of Canada), diphenylphosphine, diphenyl phosphonate (Eastman), diphenylarsine (Alfa), and xenon difluoride (PCR, Gainesville) were used as obtained. Diphenylphosphine oxide was prepared by oxidation of diphenylphosphine (7). The n.m.r. spectra were obtained on a Varian A-56/60A spectrometer using 60 and 56.4 MHz for proton and fluorine, respectively. Chemical shifts are relative to internal tetramethylsilane and trichlorofluoromethane. Mass spectra were obtained on a Finnigan 1015 quadrupole mass spectrometer. Elemental analyses were performed by Alfred Bernhardt, West Germany.

Reaction of Diphenylphosphine with Hexafluoroacetone

Diphenylphosphine (0.56 g, 3.0 mmol) was dissolved in CFCl₃ (3 ml) and hexafluoroacetone (0.73 g, 4.4 mmol) condensed onto the solution at -196° . The reaction mixture was allowed to warm to room temperature and stirred for 15 min. Removal of volatile products left a white solid identified as 2-hydroxy-1,1,1,3,3,3-hexafluoroisopropyldiphenylphosphine, (C₆H_s)₂PC(OH)(CF₃)₂ (1), on the basis of n.m.r., mass spectrometry, and chemical reactions.

The ¹⁹F n.m.r. spectrum of 1 showed a doublet, $J_{FCCP} = 17.8$ Hz, at +69.5 p.p.m. and the ¹H n.m.r. showed a singlet (OH) at -3 p.p.m. and phenyl peaks.

1 was found to be very susceptible to oxidation to give 2, described below, and the difficulty of excluding oxygen from solvents and reaction vessels prevented satisfactory elemental analysis. Rapid hydrolysis and oxidation occurred if 1 was exposed to the atmosphere, the end products being $(C_6H_5)_2P(O)OH$, identified by its mass

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spectrum and m.p. 193° (lit. $192^{\circ}(8)$) and hexafluoroacetone hydrate. A fresh sample of 1 was always prepared when needed.

The mass spectrum of 1 was contaminated by 2; however, peaks (M = molecular ion) at m/e 352(M), 351(M - H), and 313(M - HF₂) may be assigned to 1 since they are not observed in the mass spectrum of purified 2.

Oxidation of $(C_6H_5)_2PC(OH)(CF_3)_2$ to $(C_6H_5)_2P(O)C(OH)(CF_3)_2$

A slow stream of dry oxygen gas was passed through a suspension of 1 in CFCl₃ at -23° for 6 h. Removal of CFCl₃ under vacuum left a white solid identified as 2-hydroxy-1,1,1,3,3,3-hexafluoroisopropyldiphenylphosphine oxide (C₆H₅)₂P(O)C(OH)(CF₃)₂ (2). The ¹⁹F n.m.r. spectrum showed a doublet, $J_{FCCP} = 1.5$ Hz, at + 68.4 p.p.m. The mass spectrum showed highest mass ions at m/e 368(M), 367(M – H), and 348(M – HF).

ions at m/e 368(M), 367(M - H), and 348(M - HF). Anal. Calcd. for C₁₅H₁₁F₆O₂P: C, 48.92; H, 3.01; F, 30.96. Found: C, 49.10; H, 3.04; F, 30.64.

Base-catalyzed Rearrangement of $(C_6H_5)_2P(O)C$ -

 $(OH)(CF_3)_2$ (2) to $(C_6H_5)_2P(O)OCH(CF_3)_2$ (3) The preparation of 3 has been reported previously (2). In this study, a solution of 2 in THF was monitored and found to rearrange to 3, with an approximate pseudo first-order rate constant $k_1' = 6 \times 10^{-5} \text{ s}^{-1}$ at 25°. The rate of rearrangement increased on addition of a stronger base catalyst such as pyridine. Compound 2 could be prepared by an alternate route from diphenylphosphine oxide and hexafluoroacetone. Addition of pyridine again catalyzed the rearrangement to 3.

The ¹⁹F n.m.r. of **3** showed a doublet, $J_{FCCH} = 6$ Hz, at +73.9 p.p.m. (lit. +73.0 p.p.m. in dimethylformamide (2)).

Reaction of Diphenyl Phosphonate with Hexafluoroacetone

Diphenyl phosphonate (0.5 g, 2.1 mmol) and hexafluoroacetone (0.8 g, 4.8 mmol) was sealed in an n.m.r. tube and the ¹⁹F n.m.r. spectrum recorded after 24 h. Only two doublets were observed. The doublet, $J_{FCCP} =$ 3 Hz, at +71.3 p.p.m. is assigned to $(C_6H_5O)_2P(O)C(OH)(CF_3)_2$ (4) (46%) while the doublet, $J_{FCCH} = 6$ Hz, at +74.6 p.p.m. is assigned to $(C_6H_5O)_2P(O)OCH(CF_3)_2$ (5) (54%), by comparison with the chemical shifts and coupling constants found for $(RO)_2P(O)C(OH)(CF_3)_2$ and $(RO)_2P(O)OCH(CF_3)_2$ (3). Addition of base catalysts such as pyridine, diethylamine, or *n*-butyl lithium resulted in complete rearrangement of 4 to 5, as monitored by ¹⁹F n.m.r.

Reaction of $(C_6H_5)_2PC(OH)(CF_3)_2$ with Excess Hexafluoroacetone or XeF_2

Reaction of diphenylphosphine (0.21 g, 1.1 mmol) with excess hexafluoroacetone (0.71 g, 4.3 mmol) gave a white

solid 1 as described above. On standing for 3 days at room temperature the solid dissolved to give a yellow solution. Excess hexafluoroacetone was removed under vacuum and an oily liquid remained, identified as $(C_6H_5)_2PF_2C(OH)(CF_3)_2$ (7) on the basis of n.m.r. and mass spectra.

The 19 F n.m.r. showed a doublet, $J_{FP} = 806$ Hz, at +38.5 p.p.m. assigned to the PF₂ group and a doublet, $J_{FCCP} = 5.9$ Hz, of triplets, $J_{FCCPF} = 1.5$ Hz, at +74.5 p.p.m. assigned to the trifluoromethyl groups. The mass spectrum showed characteristic ions at m/e 390(M), 389(M – H), 371(M – F), 294(M – C₆H₅F), 223(C₁₂H₁₀PF₂), 204(C₁₂H₁₀PF).

Compound 7 was also prepared by treating a solution of $(C_6H_5)_2PC(OH)(CF_3)_2$ in CFCl₃ with XeF₂ (8% in CH₃CN (6)) at -196°. The mixture was kept at -63° for 2 h and then warmed to -23° for 1 h. Removal of volatile products left behind an oily liquid which gave a ¹⁹F n.m.r. spectrum identical to 7 above.

Reaction of Diphenylarsine with Hexafluoroacetone

Diphenylarsine (0.84 g, 3.7 mmol) and hexafluoroacetone (1.54 g, 9.3 mmol) were kept in a sealed tube at 25° for 4 h. Removal of volatile products left behind a viscous liquid, identified as 2-hydroxy-1,1,1,3,3,3-hexafluoroisopropyldiphenylarsine, $(C_6H_5)_2ASC(OH)(CF_3)_2$ (6). The ¹⁹F n.m.r. spectrum showed a singlet at + 69.6 p.p.m. and the ¹H n.m.r. a singlet (OH) at -2.3 p.p.m. and phenyl peaks.

Anal. Calcd. for C₁₅H₁₁F₆AsO: C, 45.47; H, 2.80; F, 28.78. Found: C, 45.30; H, 2.95; F, 28.47.

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- A. F. JANZEN and T. G. SMYRL. Can. J. Chem. 50, 1205 (1972).
- 2. R. F. STOCKEL. Chem. Commun. 1594 (1968).
- 3. A. F. JANZEN and R. POLLITT. Can. J. Chem. 48, 1987 (1970).
- 4. W. R. CULLEN and G. E. STYAN. J. Organomet. Chem. 4, 151 (1965).
- F. RAMIREZ, C. P. SMITH, A. S. GULATI, and A. V. PALWARDHAM. Tetrahedron Lett. 2151 (1966); F. RAMIREZ, C. P. SMITH, and S. MEYERSON. Tetrahedron Lett. 3651 (1966); F. RAMIREZ, A. S. GULATI, and C. P. SMITH. J. Am. Chem. Soc. 89, 6283 (1967); R. A. MITSCH. J. Am. Chem. Soc. 89, 6297 (1967).
- 6. J. A. GIBSON and A. F. JANZEN. Can. J. Chem. 49, 2168 (1971).
- M. M. RAUHUT and H. A. CURRIER, J. Org. Chem. 26, 4626 (1961).
- L. HORNER, P. BECK, and V. G. TOSCANO. Chem. Ber. 94, 1317 (1961).

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