Chemistry

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Abstract

Full Text

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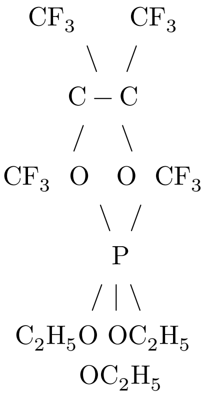
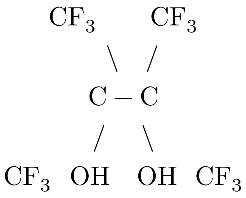
ON THE INTERACTION OF HEXAFLUOROACETONE WITH TRIETHYL PHOSPHITE

Recently we showed (1) that hexafluoroacetone reacts vigorously with triethyl phosphite, forming the cyclic phosphorane (I), whose structure was proved by hydrolysis to dodecafluoropinacol (II):

$$2(CF_3)_2CO + P(OC_2H_5)_3 \rightarrow (I) \xrightarrow[H^{\oplus}]{H_2O} (II)$$



(I)



(II)

Pinacol II can also be obtained by reduction of hexafluoroacetone with isopropyl alcohol under irradiation (2). Samples of pinacol obtained by both methods proved to be completely identical, which confirms our data on the formation of a new C–C bond in the interaction of hexafluoroacetone with triethyl phosphite.

Understandable, therefore, was our astonishment on becoming acquainted with the work of Wiley and Simmons (3), in which the interaction of hexafluoroacetone with triethyl phosphite is described as leading to the synthesis of 2-ethoxyperfluoropropylene (III):

$$\mathrm{CF_3{-}C({=}\,O){-}CF_3{+}P(OC_2H_5)_3 \rightarrow CF_3{-}C(OC_2H_5){=}CF_3{+}(C_2H_5O)_2P({=}\,}O\mathrm{)F}$$

(III)

Such a divergence in the results seemed all the more surprising because the experiment of Wiley and Simmons differed from ours only in that they introduced equimolar amounts of triethyl phosphite and hexafluoroacetone into the reaction (instead of a twofold excess of the latter in our case) and distilled the reaction mixture at atmospheric pressure (instead of distilling the cyclic phosphorane in vacuum, as we did).

In the present work we have shown that, as a result of the interaction of hexafluoroacetone with triethyl phosphite in the cold, phosphorane I is always formed; moreover, in the case of an equimolar ratio of the starting products, unreacted triethyl phosphite remains in the reaction mixture. By distillation of the mixture in vacuum, pure I was isolated in a yield of 66.7%. However, if this mixture is distilled at atmospheric pressure, then at a temperature in the flask of 170-200° decomposition occurs and indeed forms

2-ethoxyperfluoropropylene, obtained by Wiley and Simons:

$$\mathrm{(I)} \quad \xrightarrow[{[\mathrm{P(OC_2H_5)_3}]}]{170\text{–}200^\circ} \quad \mathrm{CF_3{-}C(OC_2H_5){=}CF_2 + (IV)}$$

(III)

In addition to III, small amounts of oxide (IV)* are formed, the yield of which increases markedly upon decomposition of the cyclic phosphorane in the absence of triethyl phosphite**. The boiling points of olefin III and oxide IV are practically identical; therefore we judged their formation on the basis of gas-liquid chromatography data, and in order to isolate oxide IV in pure form we separated the olefin as the dibromide.

Perfluorotetramethylethylene oxide is a colorless, highly volatile liquid with b.p. 53-54°; it is unchanged upon prolonged heating with concentrated sulfuric acid or 10% caustic potash (100°), with triethyl phosphite (160°), cyclohexene (200°), and an alcoholic solution of thiourea (120°).

The structure of oxide IV, in addition to the physical data, is confirmed by a counter-synthesis from bis(trifluoromethyl)diazomethane (V) and hexafluoroacetone (4); furthermore, oxide (IV) is formed in small amounts upon heating dodecafluoropinacol with phosphorus pentoxide:

$$\mathrm{(CF_3)_2C{=}N_2 + (CF_3)_2C{=}O} \xrightarrow[-N_2]{150^\circ} \mathrm{(IV)} \xleftarrow[\mathrm{P_2O_5}]{230^\circ\text{–}240^\circ} \mathrm{(CF_3)_2C(OH){-}C(OH)(CF_3)_2}$$

(V) (IV) (II)

Thus, the thermal decomposition of phosphorane I proceeds by two possible pathways (A and B):

$$\text{(I)} \xrightarrow{A} \text{(IV)} + (C_2H_5O)_3PO$$

$$\text{(I)} \rightleftarrows \text{zwitterionic form} \xrightarrow{B} (CF_3)_2C{=}O + \text{[intermediate]}$$
$$\downarrow$$
$$CF_3{-}C(OC_2H_5){=}CF_2 + (C_2H_5O)_2P(O)F$$
$$\text{(III)}$$

* Oxide IV was not detected in work (3).

** At the same time hexafluoroacetone is also liberated, which, naturally, could not be detected in the presence of triethyl phosphite, with which it reacts instantaneously.

Thus, the above shows that Wiley and Simmons (3), in the reaction of hexafluoroacetone with triethyl phosphite, likewise obtained cyclic phosphorane I, but decomposed it during distillation and ultimately obtained one of the possible decomposition products—2-ethoxyperfluoropropylene III.

Experimental Part

Triethoxyperfluorodimethylbutylenedioxophosphorane (I). To 9 g of hexafluoroacetone at −78°, 8.8 g of triethyl phosphite was gradually added. Distillation gave 3.5 g of triethyl phosphite and 9 g (66.7% of theory) of phosphorane I with b.p. 63–64°/1 mm, n_D^{20} 1.357. Lit. (1): b.p. 61–62°/0.5 mm, n_D^{20} 1.3555.

Decomposition of phosphorane I. A) In a Würtz flask equipped with a descending condenser and a trap (−78°), 88 g of phosphorane I was heated. At a bath temperature of 170–200°, decomposition occurs. In the trap 18.5 g of hexafluoroacetone was collected, identified as the dianiline salt of the hydrate of hexafluoroacetone (5). The distillate was treated for 20 h with an excess of bromine. From the resulting mixture, 9.6 g (17.2%) of perfluorotetramethylethylene oxide (IV), b.p. 53–54°, was removed on a column.

Found, %: C 23.01; F 72.59
$C_6F_{12}O$. Calculated, %: C 22.81; F 72.15

^{19}F NMR spectrum: singlet (CF_3).

Gas-liquid chromatography (on 3 columns with different liquid phases) showed the identity of oxide IV with the product obtained from hexafluoroacetone and bis(trifluoromethyl)cyclodiazomethane (4). From the residue after removal of oxide IV, 7.5 g (12.6%) of 2-ethoxyperfluoropropylene dibromide was isolated, b.p. 43–44°/15 mm.

Found, %: C 18.5; H 1.88; F 28.78
$C_5H_5Br_2F_5O$. Calculated, %: C 17.85; H 1.49; F 28.27

B) On heating a mixture of 8.5 g of phosphorane I and 2.8 g of triethyl phosphite to 170–200°, 3.3 g of liquid with b.p. 53–54° was obtained which, according to gas-liquid chromatography, consists of 2-ethoxyperfluoropropylene III (~ 90%) and perfluorotetramethylethylene oxide IV (~ 10%). The b.p. of 2-ethoxyperfluoropropylene is 53–54° (3).

Dodecafluoropinacolone (II). More simply than by the previously described method (1), and in better yield (72%), dodecafluoropinacolone can be obtained from the acid formed upon sulfuric-acid hydrolysis of phosphorane I, by distilling it over concentrated sulfuric acid. The melting point of the adduct of pinacolone II with dioxane, 78–80°, gives no depression of the melting point when mixed with the adduct of dodecafluoropinacolone obtained by counter synthesis according to the described procedure (2)*.

Pinacolone II distills over P_2O_5 without decomposition; however, at 230–240° (10 h) partial resinification occurs; from the reaction mixture, unreacted pinacolone (identified as the adduct with dioxane) and a small amount of oxide IV, identified by gas-liquid chromatography, were isolated.

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* Along with dodecafluoropinacolone, hexafluoroisopropyl alcohol is formed in this process (identified by gas-liquid chromatography), which is not reflected in

work (2).

Note: Figure translations are in progress. See original paper for figures.

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