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Studies on Organic Fluorine Compounds. XI.[1] Reaction of Arylfluorophosphoranes with Alcohols[2]

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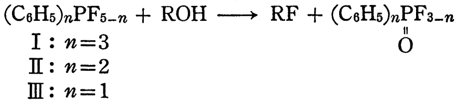
Reaction of phenyltetrafluorophosphorane (III) with 1-pentanol (IV) or 2-pentanol (V) resulted in the formation of olefins and fluoroalkanes considered to have been formed *via* the olefins. This is in contrast with the fact that the reaction of difluorotriphenylphosphorane (I) and diphenyltrifluorophosphorane (II) with IV and/or V preferentially gives fluoroalkanes thought to have been formed by direct fluorination of the alcohols. The experimental results were investigated by the stereochemistry of phosphorus.

We have earlier reported that difluorotriphenylphosphorane (I) and diphenyltrifluorophosphorane (II) could be used as the fluorinating agent in the conversion of alcohols to alkyl fluorides in one step and that II was far better than I in reacting at a lower temperature than I and in being able to be synthesized economically.[4]

In the present series of work, reactivity of phenyltetrafluorophosphorane (III), one of these fluorinating agents, with alcohols was examined. Fluorination of some trimethylsilyl ether with III was studied recently by Robert, *et al.*[5] We here report our results of the direct reaction of III with 1-pentanol (IV) and 2-pentanol (V), and some speculations on the mechanism of this reaction in order to explain the difference in reactivity of these three kinds of reagents (I, II, and III).



$$(C_6H_5)_nPF_{5-n} + ROH \xrightarrow{-HF} RF + (C_6H_5)_nP(=O)F_{3-n}$$

I : $n=3$
II : $n=2$
III : $n=1$

Chart 1

III can be prepared in a good yield by the method reported in literature.[6] The reaction conditions were the same as those in the case of the two reagents already reported except that carbon tetrachloride was used as solvent instead of acetonitrile, since III is sparingly soluble in the latter, which is decomposed by III; *i.e.*, the alcohol and about twofold moles of III were shaken in a stainless steel autoclave at *ca.* 80° for about 10 hr. After the reaction, the product was analyzed by gas chromatography; 8.3% of 1-fluoropentane (VI), a trace of 1-pentene (IX), 14% of 2-pentene (X), and 25% of a mixture of 2-fluoropentane (VII) and 3-fluoropentane (VIII) were obtained from IV. On the other hand, 11% of X and 39.6% of a mixture of VII and VIII were obtained from V. In these cases, separation of VII and VIII by gas chromatography was incomplete and their composition was estimated from the following method. Reaction of X and anhydrous hydrogen fluoride gives two products corresponding to two peaks with retention time equal to those of VII and VIII. The ions corresponding to these two peaks in gas chromatographic mass spectra show M^+ of m/e 90 and their fragment patterns indicate them to be the corresponding fluoropentanes. From

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1) Part X: Y. Kobayashi, I. Kumadaki, S. Taguchi, and Y. Hanzawa, *Chem. Pharm. Bull.* (Tokyo), **20**, 1047 (1972).
2) Presented at the 92nd Annual Meeting of the Parmaceutical Society of Japan, Osaka, April 1972.
3) Location: *3-20-1 Kitashinjuku, Shinjuku-ku, Tokyo.*
4) *a*) Y. Kobayashi and C. Akashi, *Chem. Pharm. Bull.* (Tokyo), **16**, 1009 (1968); *b*) Y. Kobayashi, C. Akashi, and K. Morinaga, *ibid.*, **16**, 1784 (1968).
5) D.V. Robert and J.G. Riess, *Tetrahedron Letters*, **1972**, 847.
6) R. Schmutzler, *Inorg. Chem.*, **3**, 410 (1964).

the ^{19}F-nuclear magnetic resonance (NMR) spectra, VI was identified with the compound synthesized by another route, and the position and splitting pattern of the signals of VII and VIII were identical with those of the two signals in ^{19}F-NMR spectra of the mixture obtained from the reaction of X and anhydrous hydrogen fluoride.

From these results, mechanism of the formation of these products was assumed to be as shown in Chart 2. In the case of IV, the intermediate (XI) would be formed first, a part of which may be converted to VI. But the majority of XI would form IX by dehydration, which would, by further isomerization, be converted to X, and addition of hydrogen fluoride generated in the first step of reaction to IX and/or X would give VII and VIII.

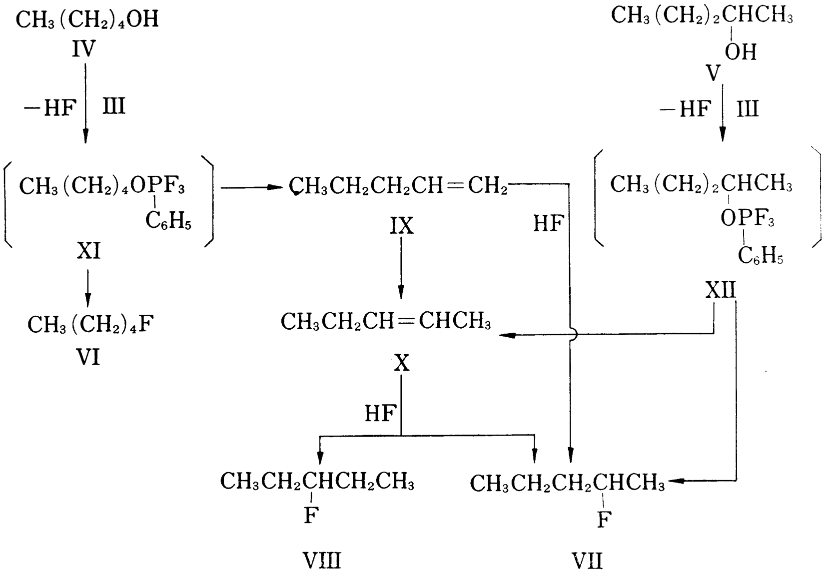

Chart 2

This assumed mechanism would be supported by the facts that the corresponding olefins are not formed from alkyl fluorides under the same conditions and that the mixture of VII and VIII was obtained by the reaction of X and hydrogen fluoride as iterated above. These experimental results showed that the reaction of III with alcohols was accompanied by the formation of olefins and reactions passing through olefins. It would be necessary to make the reaction conditions equal in each case in order to compare the reactivity of III with that of I or II. Therefore, reaction of II with IV was carried out using carbon tetrachloride as a solvent, and 42% of VI was obtained as the main product, with only a trace of olefins, VII, and VIII. This fact indicates the difference in the reactivity of III from that of I or II is not due to the difference in the solvents used.

Considerations will now be made on the reason for the difference in their reactivity. In general, pentavalent phosphorus compounds are said to take the trigonal bipyramidal structure.[7] If the first step in this reaction were to be the substitution of the fluorine atom with the alkoxyl group, the intermediate alkoxyfluorophenylphosphorane should take the trigonal bipyramidal structure, and it would be more stable when the phenyl and/or alkoxy groups are placed in an equatorial position by the effect of steric hindrance and difference in the electron negativity between these groups and fluorine atom.[7,8] Based on these assump-

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7) E.L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

8) D. Gorenstein and F.H. Westheimer, *J. Am. Chem. Soc.*, **92**, 634 (1970); D. Gorenstein, *ibid.*, **92**, 644 (1970).

tions, the intermediates in the reaction of the foregoing three reagents with alcohol would be as depicted in Fig. 1.

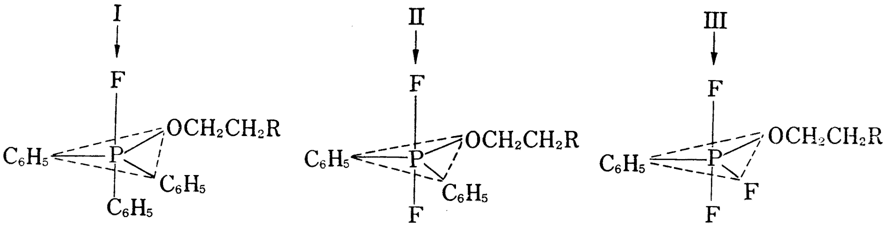
XIII XIV XV

Fig. 1

In the case of I and II, the fluorine atom would be only in apical position, and the P-F bond and P-OCH_2CH_2R bond would be in right angles to each other. In the case of III, however, there are both apical and equatorial fluorine atoms and the equatorial P-F bond would make a 120° angle with P-OCH_2CH_2R bond. The relationship between the fluorine atom and OCH_2CH_2R group will be considered with the intermediate from phenyltetrafluorophosphorane. As shown in Fig. 2, when the angle formed by F-P-O is a right angle, fluorine will attack the α-carbon atom in the form close to the transition state in the Wittig reaction and alkyl fluoride will be formed. On the other hand, when this angle is 120°, the fluorine atom would attack the β-hydrogen *via* the six-membered transition state, and an olefin would be formed. In the case of the intermediate (XV) from phenyltetrafluorophosphorane, the two foregoing relationships can be assumed in its transition state, but the six-membered ring structure (XVb) would be preferentially formed due to its stability and the olefin would be formed. On the other hand, when the reaction passes through the intermediates XIII and XIV, the six-membered transition state cannot be formed, the olefin would be difficult to be formed, and alkyl fluoride will be formed in a good yield.

It was assumed that the difference in the reactivity of these fluorophosphoranes with alcohols is primarily due to the stability of configuration of alkoxyfluorophenylphosphoranes formed as the intermediate of this reaction, and secondarily to the stability of the transition state of these intermediates undergoing decomposition into the respective products.

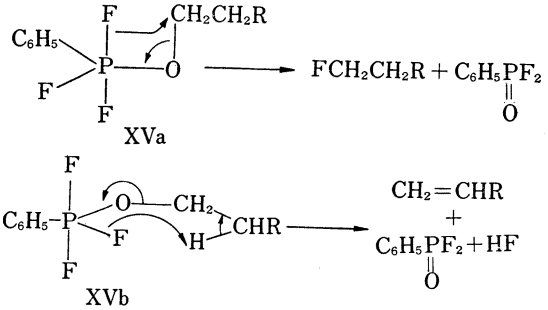
XVa XVb

Fig. 2

Experimental

Reaction of Phenyltetrafluorophosphorane (III) with 1-Pentanol (IV) in CCl_4——A mixture of 1.76 g of IV, 5.5 g of III, and 15 g of CCl_4 was stirred in SUS-27 autoclave at 80° for 10 hr and the cooled reaction mixture was washed with aq. NaOH solution. The organic layer was submitted to gas chromatography[9] and showed peaks with retention time of 1.5, 1.8, 3.4, 4.3, and 5.6 min. The first, second, and fourth peaks agreed with the retention time of commercial 1-pentene (IX), 2-pentene (X), and 1-fluoropentane (VI) synthe-

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[9] Shimadzu Model GC-1C gas chromatograph, with a column (2 mm×3.0 m), 15% diethylene glycol succinate, 27.5°. Carrier: N_2, 0.8 atm.

sized by another route described below. The third peak agreed with that of a mixture of 2-fluoropentane (VII) and 3-fluoropentane (VIII) obtained by the reaction of X and HF described below.[10] The fifth peak corresponded to CCl_4. Further, gas chromatographic mass spectrum[11] indicated that the third peak had m/e 90 (M^+) and its mass pattern agreed with that of VII and/or VIII synthesized by another route. The mass spectrum of the fourth peak showed the highest mass number of m/e 70 ($M^+ - HF$), and its mass pattern agreed with that of VI synthesized by another route.

From the foregoing organic layer, low-boiling fraction was concentrated by using a vacuum line (at 0.5 Torr) and its ^{19}F-NMR spectrum was measured in CCl_4. Three multiplet signals appeared at δ: 109, 119.6, and 157.6 (ppm).[12] The first and second signals agreed with the chemical shift and splitting pattern of the two signals of a mixture of VII and VIII synthesized by another route, and the last signal was the same as that of VI synthesized by another route.

The foregoing organic layer was quantitatively determined by gas chromatography. (The yields of products were corrected using internal standards whose relative sensitivities were known.) The yield of IX was a trace, and 14.2% of X, 25.3% of VII + VIII, and 8.8% of VI were found.

Reaction of Phenyltetrafluorophosphorane (III) with 2-Pentanol (V) in CCl_4——A mixture of 1.76 g of V, 5.5 g of III, and 15 g of CCl_4 was treated in the same manner as above. Gas chromatographic analysis of the reaction mixture indicated peaks corresponding to IX (11%), VII + VIII (39.6%), and CCl_4.

Reaction of 2-Pentene with HF——A mixture of 1.6 ml of X and 1 ml of HF was treated in a Hastelloy autoclave at 0° for 2.5 hr, the reaction mixture was washed with aq. NaOH solution, and the organic layer was analyzed by gas chromatography. The two peaks that appeared agreed in retention time and gas chromatographic mass spectral patterns with those of X and a mixture of VII and VIII. The ^{19}F-NMR spectrum of this mixture showed two signals whose chemical shift and splitting pattern agreed with those of the signals at δ: 109 and 119.6 stated above.

Reaction of Diphenyltrifluorophosphorane (II) with 1-Pentanol (IV) in CCl_4——A mixture of 0.36 g of IV, 2.17 g of II, and 5 g of CCl_4 was treated at 150° for 10 hr and the reaction mixture was treated in the conventional manner. Gas chromatographic analysis of the reaction mixture indicated that the retention time of the peak that appeared before that of CCl_4 and the mass spectral pattern in the gas chromatographic mass spectrum agreed with the peak with retention time of 4.3 min in the gas chromatography of the mixture obtained by the reaction of IV with III. Gas chromatographic analysis showed the yield of VI to be 42% and peaks corresponding to substances other than that were only in a trace. The ^{19}F-NMR spectrum of this mixture showed a signal agreeing in chemical shift and splitting pattern of the signal at δ: 157.6 of the mixture obtained by the reaction of IV with III.

Acknowledgement A part of this work was carried out at Yawata Chemical Industry Company Laboratories. We express our sincere gratitude to their cooperation.

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10) This peak separated into two peaks closely associated with one another by a column filled with polyethylene glycol.

11) Hitachi Model K53 (GC), RM-7L (MS), with a packing of 15% diethylene glycol succinate.

12) $C_6H_5C\underline{F}_3 = 0$ ppm (as an internal standard).