Difluorophenylphosphoranes Containing Four-Membered Rings[1]

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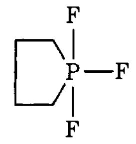
Abstract: The preparation of difluorophenylphosphoranes containing four-membered rings is described. The variable-temperature ^{1}H and ^{19}F NMR spectra of these substances indicate that the favored structure is one in which the four-membered ring spans an apical and an equatorial position of a trigonal bipyramid and the fluorines occupy an equatorial and an apical position with the phenyl in an equatorial position. Rapid switching of the fluorine positions and of the ring carbon positions occurs at the lowest temperatures investigated. In one case a minor conformer was observed, and it was concluded that this substance has the two fluorines in apical positions with the ring spanning two equatorial positions.

Studies of the chemistry and structures of various cyclic phosphoranes have been of considerable help in elucidating those factors which govern the reactivity and properties of phosphoranes in general.[2] Two generalizations have arisen from these and other investigations. The first, the "element effect", postulates that in a trigonal-bipyramidal phosphorane the most electronegative groups will prefer to adopt apical dispositions.[3] The second, the "ring strain effect", suggests that there will be less strain in rings which span apical-equatorial positions.[4] The "ring strain effect" is thought to be important in compounds containing five-membered and smaller rings. It should be noted, however, that compound **1** exists at low temperature with the ring spanning two equatorial positions,[3] and compound **2**, at room temperature, also has the ring diequatorial.[5] On the other hand, compound **3**, at room temperature, shows no tendency to allow the ring to adopt a diequatorial disposition on the NMR time scale.[6] One major difference between compounds **1** and **2** and **3** is, of course, that in the first two, carbons are bonded to phosphorus vs. oxygens in **3**, and thus the lower electronegativity of carbon favors the diequatorial placement of the ring. It is not clear what the differences in ring strain are for the two different ring systems.



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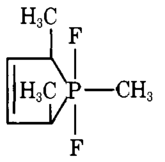

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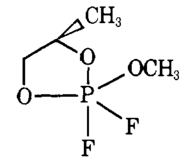

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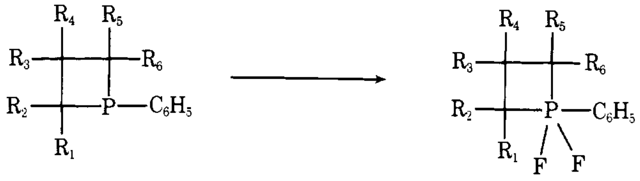
Recently it has been shown that spirocyclic phosphoranes may often prefer to exist as square pyramids rather than trigonal bipyramids.[7] These observations serve to reopen many questions concerning the structures of phosphoranes. As yet no acyclic or monocyclic phosphorane has been found which has as its ground state the square-pyramidal structure; however, such structures are not precluded, and in view of the new evidence it would seem that they must be considered in any total evaluation of a particular system.

The preparation of difluorophosphoranes from trivalent phosphorus compounds has been made relatively easy by introducing trifluoromethyl hypofluorite (**4**), bis(trifluoromethyl) peroxide (**5**), and to a lesser extent bis(trifluoromethyl) disulfide (**6**) as reagents.[5] These reagents react with the trivalent phosphorus compounds under very mild conditions to give ultimately the difluorophosphoranes and gaseous products. The three phosphoranes **10**, **11**, and **12** have been prepared in solution by these methods.

Results and Discussion



7 $R_1 = R_2 = R_5 = R_6 = CH_3$; $R_3 = R_4 = H$ 10
8 $R_1 = R_2 = R_3 = R_4 = CH_3$; $R_5 = R_6 = H$ 11
9 $R_1 = R_2 = R_3 = R_5 = R_6 = CH_3$; $R_4 = H$ 12

These substances have been characterized primarily by variable-temperature studies of their ^{1}H, ^{19}F, and ^{31}P NMR spectra. For example, the ^{1}H NMR spectrum of **10** at ambient temperature showed a doublet at δ 1.37 (J_{PCCH} = 19 Hz), another doublet was found at δ 1.68 (J_{PCCH} = 35 Hz), and a complex absorption was found between δ 7.3 and 8.0. The ratio of these absorptions was 12:2:5. The ^{1}H NMR spectrum at ca. −100° showed three doublets in the region for absorptions of hydrogens of methyl groups. These are tentatively assigned as δ 1.56 (J_{PCCH} = 15.5 Hz), 1.47 (J_{PCCH} = 25 Hz), and 1.14 (J_{PCCH} = 22 Hz). The ^{31}P NMR spectrum at ambient temperature consisted of a very broad mound centered at about 0 ppm relative to 85% phosphoric acid. Similarly, the ^{19}F NMR spectrum at ambient temperature consisted of a broad moundlike absorption centered at 50 ppm relative to trichlorofluoromethane. These data are consistent with a series of structures for **10** which are undergoing rapid intramolecular interconversion on the ^{1}H NMR time scale and which render the hydrogens of all four methyl groups magnetically equivalent as they do the methylene hydrogens. The ^{31}P and ^{19}F NMR spectra are also consistent with this picture; however, on their NMR time scales the exchange process is very near or equal to the coalesence temperature. At ca. −100° the ^{31}P NMR spectrum had two triplets at δ −3.0 (J_{PF} = 932 Hz) and δ +30 (J_{PF} = 769 Hz); these two absorptions had relative areas of 2.3:1. The ^{19}F NMR spectrum at ca. −95° had two doublets at δ +36.3 (J_{PF} = 775 Hz) and δ +63.5 (J_{PF} = 933 Hz); these two absorptions had relative areas of 1:2.4.

Compound **11**, at ambient temperature, had a ^{1}H NMR spectrum with a singlet at δ 0.8, a doublet at δ 1.35 (J_{PCCH} = 21 Hz), and a doublet at δ 2.75 (J_{PCH} = 13 Hz). A complex multiplet was found between δ 7.4 and 8.2. The ratio of the areas of these absorptions was 6:6:2:5. The singlet is assigned to the hydrogens of the R_3 and R_4 methyl groups, the six-hydrogen doublet to the hydrogens of the R_1 and R_2 methyl groups, and the two-hydrogen doublet to the hydrogens of the methylene group; the remaining absorption is due to the aromatic hydrogens. The ^{31}P NMR spectrum displayed a very broad diffuse absorption centered at δ 0. Similarly, the ^{19}F NMR spectrum showed a broad absorption centered at δ 51.

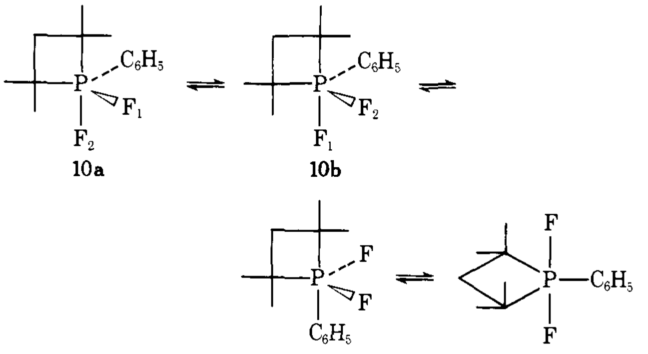
These data can be interpreted in a manner entirely analogous to that used for **10**, i.e., intramolecular exchange between structures which make the hydrogens of the R_1 and R_2 methyl groups equivalent. The exchange process also makes the hydrogens of the R_3 and R_4 methyl groups and the hydrogens of the methylene group equivalent.

The low-temperature ^{31}P NMR spectrum of **11** at −80° consisted of a doublet, each line of which was split into a doublet. The doublet was centered at δ 7.5 (J_{PF_1} = 973 Hz) and (J_{PF_2} = 872 Hz). The ^{19}F NMR spectrum at −80° had one doublet of doublets at δ +46 (J_{PF_2} = 875 Hz and $J_{\mathrm{F}_1\mathrm{PF}_2}$ = 15.7 Hz); another doublet of doublets was found at δ 58.6 (J_{PF_1} = 987 Hz and $J_{\mathrm{F}_1\mathrm{PF}_2}$ = 15.7 Hz). The latter splitting was poorly resolved but recognizable. The ^{1}H NMR spectrum at −60° had a three-hydrogen singlet at δ 0.5, another at 0.95, a three-hydrogen doublet at δ 1.24 (J_{PCCH} = 24.5 Hz), and another at δ 1.55 (J_{PCCH} = 18.5 Hz). The hydrogens of the methylene group were found as an apparent doublet at δ 2.79 (J_{PCH} = 14 Hz).

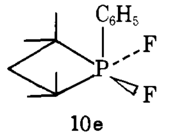
The ^{1}H NMR spectrum of **12** at ambient temperature was quite complex; however, the ratio of aliphatic to aromatic protons was 16:5 as expected. The ^{19}F NMR spectrum consisted of a doublet of rather broad absorptions centered at δ 58.8 (J_{PF} = 922 Hz). The ^{31}P NMR spectrum showed a triplet at δ −1.0 (J_{PF} = 911 Hz).

At −90° the ^{19}F NMR spectrum showed two doublets, one at δ 58.8 (J_{PF} = 922 Hz) and +71.2 (J_{PF} = 900 Hz). The relative ratio of these absorptions was 4:1. The ^{31}P NMR had the original triplet, and a new triplet was found at δ −11.2 (J_{PF} = 909 Hz).

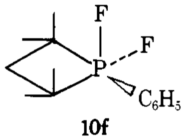
The traditional structures, which would be considered to account for the low-temperature NMR spectra for **10**, are illustrated (see **10a–d**). To these one should add square-pyramidal structures **10e–h**. All of these structures are idealized, and bond angle deviations and lengths can certainly not be discounted. The low-temperature NMR data for **10** show quite clearly that there are two conformers present, and they are interconverting slowly on the respective NMR time scales. The major component has equivalent fluorines and two kinds of methyl group hydrogens, whereas the minor component has equivalent fluorines, and all of the methyl group hydrogens are equivalent. In the case of compound **11**, only one conformer was observed at low temperatures. Given the sensitivity of the NMR measurements, certainly small amounts of other conformers could have not been detected. The conformer of **11** at low temperatures has nonequivalent fluorines which are coupled to each other and which have rather different chemical shifts and coupling constants. A tentative interpretation would be that one fluorine is equatorial or spends most of its time in an equatorial position, while the other is apical or spends most of its time in an apical position of a trigonal bipyramid. Another interpretation might involve one fluorine in a basal position and another in an apical position of a square pyramid. Positional switching could occur; however, each fluorine would have to spend most of its time in one position.



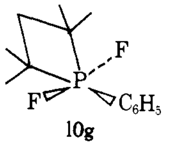
10a **10b** **10c** **10d**



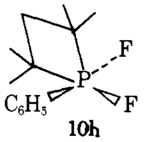
10e



10f

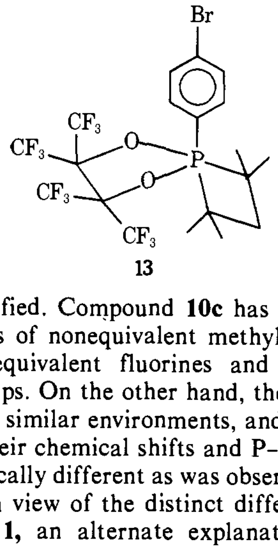


10g



10h

Recently it has been shown that compound **13** exists as a square pyramid in the crystalline state.[8] If it is assumed that the major conformer of **10** and the conformer of **11**, which was found at low temperatures, have the same general structures as **13**, then the NMR data are qualitatively satisfied. Compound **10c** has equivalent fluorines and two pairs of nonequivalent methyl groups. Compound **11f** has nonequivalent fluorines and four nonequivalent methyl groups. On the other hand, the two fluorines of **11f** occupy very similar environments, and it would be strange, indeed, if their chemical shifts and P–F coupling constants were so radically different as was observed.



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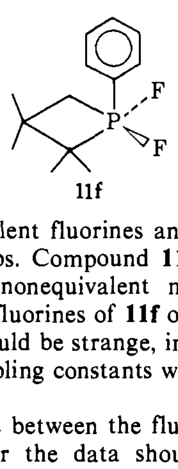
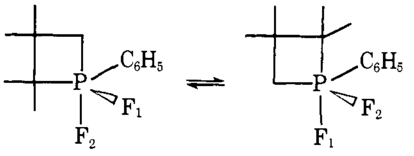


11f

In view of the distinct differences between the fluorines of **11**, an alternate explanation for the data should be sought. Not one of the structures **10f**, **10g**, or **10h** satisfies the NMR spectral data for the major conformer of **10**. It has also been pointed out by Holmes[7] that electronegative groups will prefer basal positions of square pyramids, and small rings will prefer to span two basal positions. The basal-basal angle is ca. 88° while the basal-axial angle is ca. 105°. These concepts and the conclusions reached above strongly suggest that the major conformers of **10** and **11** are not square pyramids.

Of the remaining structures for **10**, **10a** and **10b** can accommodate the data provided they are undergoing rapid interconversion on the NMR time scale. Similarly, interconversion of **11a** and **11b** can account for the low-temperature NMR data for **11**. It is required that **11a** and **11b** are in rapid equilibrium, and the equilibrium constant favors one form over the other. The latter requirement is necessary to explain the considerable difference in coupling constants and chemical shifts between the two fluorines. The values of



11a **11b**

these parameters fall in the range observed for an equatorial fluorine in one case and an apical fluorine in another.[9]

The two compounds from **12**, which were shown to be present at low temperatures by NMR spectroscopy, can have structures analogous to **10a, 10b** and **11a** and **11b**, except in this example there are two isomers, one where the methyl and phenyl groups are trans to each other and one where they are cis.

The minor conformer from **10** has a low ^{19}F chemical shift which is typical of apical fluorines, and the P-F coupling constant is in the range found for apical fluorines.[9] On this basis and the agreement with the ^{1}H NMR spectrum, structure **10d** is assigned to the minor conformer. Such a structure is in complete agreement with the "element effect" where carbons occupy the equatorial positions and fluorines occupy apical positions. The structure does violate the "strain rule"; however, no evidence has ever been presented which indicates that a four-membered ring containing only carbon and phosphorus cannot adopt a diequatorial disposition.

Recently Musher and Agosta[10] have suggested that the interpretation of the low-temperature NMR data for **10**[11] does not require that **10d** be the minor conformer. The NMR data for **11** and **12** were not available to them, so they did not know that the data for **11** eliminate their favored alternate explanation.

The barrier to interconversion of **10a** and **10b** to **10d** can be explained in terms of the Berry mechanism for pseudorotation,[12] which requires that **10c** be formed as an intermediate for such an interconversion to occur. The instability of **10c** relative to the other conformers can be related to the "element effect". Clearly placing the fluorines diequatorial and the phenyl group apical is going to require an input of energy.

The results of this study serve to further quantify the relative importance of the "strain" and "element" effects as they apply to the structures of phosphoranes. It should be noted that Tripett[13] and his coworkers have used four-membered ring phosphoranes to determine relative apicophilicities of various groups. Their studies also involve placing the four-membered ring diequatorial.

Experimental Section

Phosphorus and fluorine spectra were obtained with an HA-100, while proton spectra were obtained with HA-100, A-60, and T-60 spectrometers. Compounds **8** and **9** were prepared by standard literature procedures.[14] Trifluoromethyl hypofluorite, bis(trifluoromethyl) peroxide, and bis(trifluoromethyl) disulfide were obtained from Peninsular Chem Research.

Preparation of 2,2,4,4-Tetramethyl-1-Phenylphosphetane Oxide (14). To a suspension of aluminum chloride, 33.6 g (0.25 mol) in 200 ml of methylene chlorine, was added at 5° 44.9 g (0.25 mol) of phenyldichlorophosphine followed by 24.8 g (0.25 mol) of 2,4-dimethyl-2-pentene in 75 ml of methylene chloride. The mixture was allowed to warm to room temperature where it was allowed to stand for 2 days. The mixture was poured into 1 l. of ice water, the layers were separated, and the aqueous layer was washed with two 50-ml portions of methylene chloride, which were added to the original organic mixture. The methylene chloride was removed by distillation, and water was finally removed by azeotropic distillation with benzene. There was obtained 57.6 g of crude product, which upon distillation at 122-124° (0.025 mm) yielded 25 g (45.5%) of material which solidified upon standing. This solid was recrystallized from cyclohexane, mp 93-97°, ^{1}H NMR (CH_2Cl_2) δ 1.16 (d, J = 18.8 Hz, 6 H), 1.55 (d, J = 15.6 Hz, 6 H), 2.1 (m, 2 H), and 7.7 (m, 5 H); ^{31}P NMR (CH_2Cl_2) δ −51.

Anal. Calcd for $C_{13}H_{19}OP$: C, 70.27; H, 8.55. Found: C, 69.95; H, 8.61.

Preparation of 7. To a mixture of 11.1 g (0.05 mol) of **14** and 5.1 g (0.05 mol) of triethylamine in 60 ml of benzene at 5° was added, with stirring and under an argon atmosphere, 6.8 g (0.05 mol) of trichlorosilane in 20 ml of benzene. The reaction mixture was allowed to warm to room temperature and was stirred overnight. After cooling to 10°, there was added to the mixture 80 ml of 20% sodium hydroxide solution. The layers were separated, and the organic phase was concentrated. The residual oil was distilled at 71-73° (0.02 mm) to yield 4.5 g (43%) of product: ^{1}H NMR (CH_2Cl_2) δ 1.25 (d, J = 6 Hz, 6 H), 1.43 (d, J = 19.5 Hz, 6 H), 2.3 (m, 2 H), 7.22 (m, 5 H); ^{31}P NMR (neat or CH_2Cl_2) δ −44.

Preparation of 10. The phosphetane **7**, 0.51 g in 2 ml of methylene chloride, was added dropwise to a stirred solution of 0.54 g (ca. 25% excess) of **5** in 1 ml of methylene chloride at −78°. Initially two layers formed. These slowly became miscible as the reaction mixture was stirred at −78° for ca. 30 min. The reaction mixture was allowed to warm to room temperature, and the ^{1}H NMR spectrum was recorded. It showed that the reaction mixture consisted primarily of the desired phosphorane **10.** The same product resulted from the reactions of **7** with **4** and **6**. Compound **10** can be distilled, bp 74-77° (0.2 mm). It has been hydrolyzed to the known corresponding oxide. Compound **10** has the following infrared absorptions (carbon tetrachloride solution): ν_{max} 2980, 1450, 1215, 951 cm^{-1} and as a film ν_{max} 2960, 1450, 1120, 952 cm^{-1}. Attempted analysis of **10** gave a satisfactory hydrogen content; however, the carbon content was high by 0.8%.

Preparation of Compounds 11 and 12. These materials were prepared in solution and used as such.

References and Notes

(1) This research has been supported by the National Science Foundation and by a Public Health Service Research Grant No. CA-10737 from the National Cancer Institute.

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