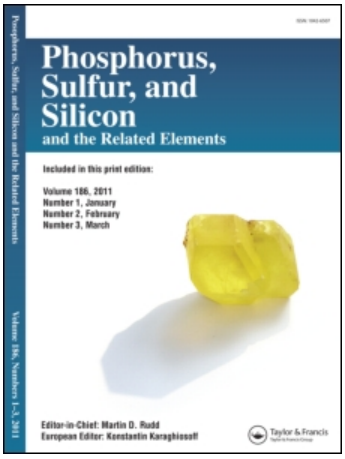

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SOME MONOCYCLIC AND SPIROCYCLIC FLUOROPHOSPHORANES CONTAINING 6- AND 7-MEMBERED RINGS

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SOME MONOCYCLIC AND SPIROCYCLIC FLUOROPHOSPHORANES CONTAINING 6- AND 7-MEMBERED RINGS

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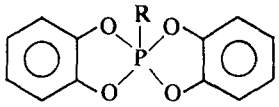
The reaction of 2,2-dimethyl-(1,8-naphtho[c,d])-1,3,2-dioxysilenin (3) and 2,2-dimethyldibenzo-1,3,2-dioxysilepin (4) with $(C_6H_5)_2PF_3$ gave the expected monocyclic fluorophosphoranes. Reaction of the same siloxy compounds with PF_5 gave products which could not be purified but whose ^{19}F nmr spectra suggested that the desired spirocyclic compounds were present in the impure products. Reaction of the siloxy compounds with $C_6H_5PF_4$ did not yield identifiable products. The ^{19}F nmr spectra of the products obtained are discussed and structures are tentatively assigned.

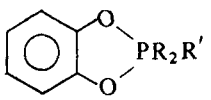
Doak and Schmutzler[1] have studied the reaction of *o*-phenylenedioxybis-(trimethylsilane) with phosphoranes of the type R_nPF_{5-n} where n = 0, 1, 2, or 3. Where n = 0 or 1 spirans of the type **1** were obtained.



1

where n = 0, R = F (**a**); where n = 1, R = CH_3 (**b**) or C_6H_5 (**c**).

Where n = 2 or 3 monocyclic phosphoranes of the type **2** were isolated. Compound 1a was of particular



2

where n = 2, R = CH_3, R′ = F (**a**); R = C_6H_5, R′ = F (**b**), or R = $-CH_2CH_2CH_2CH_2-$, R′ = F (**c**). Where n = 3, R = R′ = $-CH_2CH_2CH_2CH_3$ (**d**).

interest in that the ^{19}F nmr spectrum strongly suggested that the single fluorine atom occupied the equatorial position of a trigonal bipyramid (TBP)[2] contrary to the Muetterties polarity rule.[3] This reasoning was based on the high chemical shift (δ = 70.4 ppm referred to $CFCl_3$) and to the large P-F coupling constant (J_{P-F} = 1011 Hz). The chemical shift and coupling constant were similar to values found for equatorial fluorines in compounds known to possess an equatorial fluorine atom (e.g. $(C_6H_5)_2PF_3$).[4] This violation of the Muetterties polarity rule was ascribed to the rigidity of the *o*-phenylenedioxy ring system which could only be accommodated in equatorial-apical positions of the TBP, forcing the fluorine into an equatorial position. Since at that time there was no evidence that the geometry of five-covalent phosphorus compounds was ever different from that of a TBP, no other structure was considered for spirans of the type **1**.

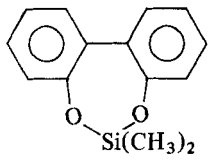
The above reasoning has now been shown to be erroneous. X-ray analysis of compound **1a** has demonstrated that its geometry is intermediate between that of a TBP and that of a tetragonal pyramid (TP), while the structure of compound **1b** is in almost complete agreement with that of a TP.[5] Other examples of deviations from TBP geometry include the compound where the oxygen atoms of compound **1b** have been substituted by sulfur atoms[6] and compound **1** where R = OC_6H_5.[7] The geometry of the latter compound has been described as a 15° turnstile rotation (TR) configuration. This nomenclature is based on the well-known TR mechanism, proposed and widely used by Ramirez and coworkers to explain certain intramolecular exchange phenomena in TBP chemistry.[8,9] For an exact description of this nomenclature, papers by Ramirez and coworkers should be consulted.[8,10] In a recent paper from Ramirez's laboratory much of our present knowledge of factors which affect deviations of phosphoranes from TBP geometry has been summarized.[11] In particular it has been noted that two

five-membered rings in a spirocyclic configuration apparently constitute a type of restriction that prevents the establishment of the regular TBP geometry. In explanation it has been suggested that, at least in 1,3,2-dioxaphospholene spirocyclic compounds, incorporation of the phosphorus atom into the spiro ring system prevents to some extent the involvement of the electrons of the oxygen in p-d π bonding, an effect which would decrease the tendency of the P atom to adopt TBP geometry.

From results described in the previous paragraph it now appears that a fluorine atom in the apical position of a TP (or a distorted TP) also gives a large chemical shift and a large J_{P-F} value and therefore such large values cannot be used as a diagnostic tool for assigning a fluorine atom to the equatorial position in a TBP.

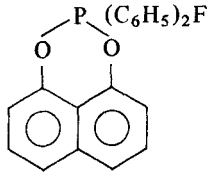
It should be noted that many of the conclusions reached by Ramirez and coworkers in their recent paper[11] are based on data obtained with the five-membered 1,3,2-dioxaphospholene ring system, whether in monocyclic or in spirocyclic compounds. Much less is known about other ring systems.[12] The present paper is concerned with pentacovalent phosphorus compounds which contain the 1,3,2-dioxy- ring system, where the rings are 6- or 7-membered. For this purpose we choose as starting materials the dioxybis(trimethylsilane) derivatives of 1,8-naphthalenediol (**3**) and *o,o'*-biphenol (**4**). These were allowed to react with PF_5, $C_6H_5PF_4$, or $(C_6H_5)_2PF_3$ under

3



4

conditions similar to those employed by Doak and Schmutzler[1] for the reaction of these phosphoranes with *o*-phenylenedioxybis(dimethylsilane). As before the course of the reaction was followed by trapping and weighing at intervals the difluorodimethylsilane formed during the reaction. With $(C_6H_5)_2PF_3$ the expected compounds **5** and **6** were readily obtained.



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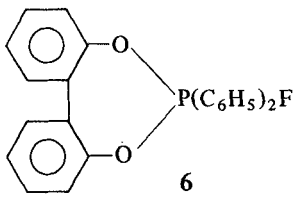
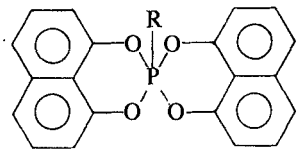


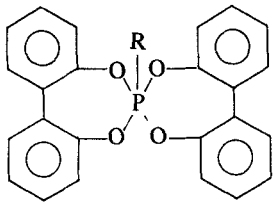
6

These were crystalline solids with sharp mp's and satisfactory elemental analyses. The ^{19}F nmr spectra (Table) yielded chemical shift and coupling constant values in agreement with TBP molecules with an apical fluorine atom.

We were much less successful in preparing the spirocyclic compounds **7** and **8**. The reaction of PF_5 with either **3** or **4** gave yields of $(CH_3)_2SiF_2$ which were

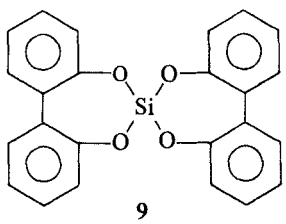


7a, R = F; **b**, R = C_6H_5



8a, R = F; **b**, R = C_6H_5

invariably less than theoretical and often did not exceed 50%. The crude reaction products were highly sensitive to atmospheric moisture as judged by the rapid loss of the ^{19}F nmr signal on exposure to the air. Accordingly all manipulations were carried out in a dry box. The crude products were only slightly soluble in common organic solvents and we were unable to obtain crystalline products from any of the solvents tried. Vacuum sublimation was also unsuccessful. Elemental analyses on the crude products or on the material obtained by dissolving the crude product in a solvent followed by partial evaporation to yield a powder, gave unsatisfactory values, but the C: F and P: F ratios obtained suggested that we had not obtained monocyclic trifluorophosphoranes as the principal product of the reaction. Several attempts to prepare **8a** by the reaction of PF_5 with the spirocyclic compound **9** gave products similar to those obtained from PF_5 and **4**.



9

In spite of our inability to obtain **7a** or **8a** in an analytically pure form we were able to dissolve a sufficient amount of both crude products in nitrobenzene or toluene to obtain satisfactory nmr signals. Both products gave sharp doublets whose chemical shifts (Table) were quite similar to the value found for **1a**. Furthermore the J_{P-F} value for compound **7a** was extremely

large (1061 Hz), even larger than that found for compound **1a** (1011 Hz). No bands other than the doublets were found in the ^{19}F nmr spectra of either compound. The results suggest that compounds **7a** and **8a** are indeed formed in the reactions of **3** and **4** with PF_5, but that it is more difficult, probably for steric reasons, to incorporate the larger naphthyl or biphenyl rings into the spiro system. Other products, possibly polymeric, are formed in the reaction and we have been unable to separate the desired spirans from the accompanying impurities.

The reaction of $C_6H_5PF_4$ with **3** or **4** was even less successful. In neither reaction did the yield of $(CH_3)_2SiF_2$ exceed 50% of the theoretical. With $C_6H_5PF_4$ and **3** a black oil was obtained from which no solid could be isolated. The same reaction with **4** gave a sticky solid, but no product with the correct analysis for **8b** could be obtained from this solid on recrystallization. Thus we have no evidence that either of the desired spirans **7b** or **8b** are formed in the reaction of $C_6H_5PF_4$ with **3** or **4**.

Some comments on the ^{19}F nmr spectra of the crude products **7a** and **8a** are in order. Both the chemical shift and J_{P-F} for compound **7a** do not differ significantly from those of the catechol compound **1a**, which has been shown by X-ray data to be a distorted TP. It seems reasonable, therefore, to suggest that compound **7a** has a similar structure to **1a**, i.e., intermediate between a TBP and a TP. Although the chemical shift of **8a** is also similar to that of **1a**, the J_{P-F} value for **8a** is in the same range as the J_{P-F} values for the monocyclic compounds **2a**, **2b**, **2c**, **5** and **6**. It seems probable then that compound **8a** more closely resembles a TBP with one ring bridging two equatorial positions and the fluorine occupying one apical position. It has previously been stated that a seven-membered ring is the smallest ring which can be placed diequatorially without any constraint.[13] It should also be noted that the biphenyl ring system is more flexible than the naphthalene ring system. Had we used siloxy compounds derived from less flexible diols, e.g., 4,5-phenanthrenediol or 4,5-fluorenediol, the resulting spirans might have resembled **7a**.

EXPERIMENTAL

The PF_5 and *o,o'*-biphenol were commercial products obtained from Ozark-Mahoney and Aldrich Chemical Company, respectively. The 1,8-napthalenediol was first prepared by the method of Lurie, Brown, and Weissberger[14] but the yield was only about 10%. We have improved the synthesis considerably although the yields are still only moderate (34%). Two of the three siloxy compounds, namely 4[15] and 9,[16] are known compounds and were prepared in this laboratory by the published methods. 2,2-Dimethyl-(1,8-naphtho[c, d])-1,3,2-dioxysilenin (**3**) is a new compound and its synthesis is described. All solvents were dried over molecular sieves before use and operations on the moisture-sensitive compounds were carried out in a dry box. The nmr spectra were determined on a Varian HA 100 spectrometer; mp's were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were by Galbraith Laboratories, Knoxville, Tennessee.

Naphthalene-1,8-diol

A mixture of 150 g of KOH and 150 g of NaOH was heated in a 1 l stainless steel beaker until fusion occurred. Sodium 1-naphthol-8-sulfonate was added to the fusion mixture in small portions with stirring. Heating and stirring were continued until the mixture turned from green to black and started to foam (250–275°). The molten mixture was poured into a stainless steel bowl and allowed to cool and solidify. The solid was crushed into small pieces and added cautiously to 700 ml of conc. HCl. The final solution was made strongly acid with HCl and boiled with decolorizing charcoal. The hot solution was filtered through glass wool which was washed with small portions of boiling water. The diol crystallized when the aqueous solution was allowed to cool. The yield was 34%; mp 135–137° (lit. 144[12]).

2,2-Dimethyl-(1,8-naphtho[c,d])-1,3,2-dioxysilenin (**3**)

Naphthalene-1,8-diol (16.0 g, 0.1 mole) and 150 ml of dry pyridine in 100 ml of anhydrous ether were placed in a 500 ml three-neck flask equipped with stirrer, addition funnel and reflux condenser protected with a drying tube. To this solution 12.8 g (0.1 mole) of $(CH_3)_2SiCl_2$ was added dropwise with rapid stirring. After the silane was all added the mixture was refluxed for two hours after which the pyridine hydrochloride was removed by filtration and washed with hot benzene. The solvents were removed from the filtrate under reduced pressure and the resulting solid was recrystallized from benzene. Yield 34%, mp 51–53°. Anal. calcd. for $C_{12}H_{12}O_2Si$: C, 66.66%; H, 5.55%. Found: C, 66.58%; H, 5.41%.

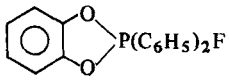
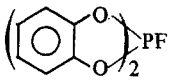
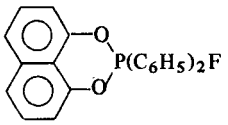
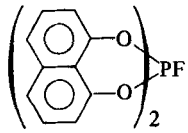
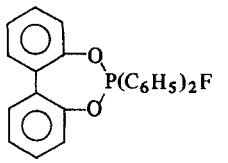
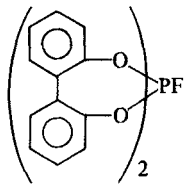
2-Fluoro-2,2-dihydro-2,2-diphenyl-(1,8-naphtho[c,d])-1,3,2-dioxaphosphorin (**5**)

It was prepared from $(C_6H_5)_2PF_3$ and **3** by the same procedure used by Doak and Schmutzler[1] for the preparation of the catechol compound except that benzene was used as the solvent. The yield of difluorodimethylsilane generated in the reaction was approximately theoretical. The yield of pure **5** after recrystallization from benzene was 15%; mp 135°. Anal. calcd. for $C_{22}H_{16}FO_2P$; C, 72.9%; H, 4.41%. Found C, 72.8%; H, 4.58%.

2-Fluoro-2,2-dihydro-2,2-diphenyldibenzo[c,e]-1,3,2-dioxaphosphepin (**6**)

This compound was prepared in a similar manner from $(C_6H_5)_2PF_3$ and **4**. The yield of difluorodimethylsilane was 100%. The yield of pure **6**, after recrystallization from CCl_4, was 31%; mp 134–138°. Anal. calcd. for $C_{24}H_{18}FO_2P$: C, 74.25%; H, 4.64%. Found: C, 74.34%; H, 4.68%.

TABLE I
^{19}F nmr data and configurations of fluorophosphoranes

Compound	δ*	J_{P-F}	Comments
	26.2 ppm	772 Hz	TBP with apical F
	70.4 ppm	1011 Hz	Intermediate between TBP and TP
	12 ppm	698 Hz	TBP with apical F
	85 ppm	1061 Hz	Intermediate between TBP and TP
	2.8 ppm	723 Hz	TBP with apical F
	72.1	736 Hz	TBP with an apical F

* Referred to $CFCl_3$.

Attempted Preparation of 2-Fluoro-2,2-spirobi (1,8-naphtho-[c,d])-1,3,2-Dioxaphosphorin (7a)

The procedure used was similar to that used for the preparation of the corresponding catechol derivative **1a**,[1] except that a Monel bomb rather than a glass tube was used. Compound **3** was placed in the bomb, an excess of PF_5 was then condensed into the bomb using liquid nitrogen and the bomb was then kept at room temperature for 48 hours. It was then reattached to the vacuum line and the Me_2SiF_2 collected in a trap cooled in "Dry Ice"-acetone. The yield of Me_2SiF_2 was 40%. The bomb was then transferred to a dry box and the contents removed. The solid obtained could not be successfully recrystallized from any common organic solvent. The reaction was also carried out by heating the bomb to 75° for 48 hours in which case the yield of Me_2SiF_2 was 90%, but the product again could not be successfully recrystallized. Anal. (crude material) calcd. for $C_{20}H_{12}FO_4P$: C, 65.57%; H, 3.27%; F, 5.19%; P, 8.45%. Found C, 63.72%; H, 4.14%; F, 3.87%; P, 5.41%. The ^{19}F nmr spectrum of the crude material is given in the table.

Attempted Preparation of 2-Fluoro-2,2-spirobi (dibenzo [c,e])-1,3,2-dioxaphosphepin (8a)

No reaction occurred when the siloxy compound **4** and PF_5 were kept at room temperature in a Monel bomb for 48 hours. Accordingly all further reactions were carried out at elevated temperatures (75–85°) for time periods ranging from 48 hours to one month. The yield of Me_2SiF_2, however, was always in the range 50–60%. The crude product was only slightly soluble in organic solvents, but did dissolve to some extent in a benzene–toluene mixture from which a solid was obtained on evaporating the solvents. Analyses of the crude products (and of the material obtained from benzene–toluene) were quite variable from one preparation to another and were never in agreement with theory.

Attempted Preparation of 2-Phenyl-2,2-spirobi (1,8-naphtho-[c,d])-1,3,2-dioxaphosphorin **7b** *and 2-Phenyl-2,2-spirobi-(dibenzo[c,e]-1,3,2-dioxaphosphepin* **8b**

The procedure used was the same as that used for the successful

preparation of compound **1c**. The reaction of **3** and $C_6H_5PF_4$ gave an intractable oil. With **4** and $C_6H_5PF_4$, the sticky solid did not give **8b** on attempted recrystallization from toluene.

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