Preparation and Nuclear Magnetic Resonance Studies of Pentacoordinated Phosphorus Compounds Containing Hexafluoroisopropoxy Groups†

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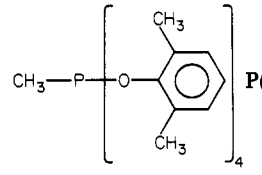
The reaction of 1,1,1,3,3,3-hexafluoroisopropyl benzenesulfenate (7) with tris(1,1,1,3,3,3-hexafluoroisopropyl) phosphite (8) yielded tetrakis(1,1,1,3,3,3-hexafluoroisopropoxy)(phenylthio)phosphorane (9). Variable-temperature ^{19}F NMR studies of 9 show that below −26 °C there are two kinds of hexafluoroisopropoxy groups. Reaction of 7 with bis(1,1,1,3,3,3-hexafluoroisopropyl) phenylphosphonite (10) yielded tetrakis(1,1,1,3,3,3-hexafluoroisopropoxy)phenylphosphorane (4). Variable-temperature ^{19}F NMR studies of this substance show that below −10 °C there are two kinds of hexafluoroisopropoxy groups. Interestingly, pentakis(1,1,1,3,3,3-hexafluoroisopropoxy)phosphorane (2) showed no separation into two resonances in its ^{19}F NMR spectrum on cooling to −95 °C. Reaction of 1,1,1,3,3,3-hexafluoroisopropyl diphenylphosphinite (11) with 7 yielded tris(1,1,1,3,3,3-hexafluoroisopropoxy)diphenylphosphorane (6). The variable-temperature ^{19}F NMR spectra of this substance showed that below 30 °C there are two kinds of hexafluoroisopropoxy groups in the ratio of 2:1. Further cooling led to three different kinds of hexafluoroisopropoxy groups in the ratio 1:1:1. The variable-temperature ^{19}F NMR spectra of all these substances are discussed in terms of intramolecular ligand reorganization processes. Other experiments involving five-membered-ring-containing phosphoranes and attempts to form hexacoordinated phosphorus compounds are discussed.

Recently a series of penta- and hexacoordinated phosphorus compounds containing trifluoroethoxy groups was prepared.[1] The method of preparation of pentacoordinated materials involved reaction of a trivalent phosphorus compound with 2 mol of trifluoroethyl benzenesulfenate. Subsequent reaction of these materials with trifluoroethoxide ion often led to the formation of hexacoordinated substances. Variable-temperature ^{19}F NMR studies of these molecules provided some information on the barriers to intramolecular ligand reorganization. It was not possible to measure barriers for oxyphosphoranes containing four or more trifluoroethoxy groups.

Earlier work had indicated that intramolecular ligand reorganization is subject to steric influences.[2] Westheimer and his co-workers[3] prepared the phosphorane 1. The



1

$P(OR_f)_5$ 2

$RP(OR_f)_4$ 3, R = CH_3; 4, R = C_6H_5

$R_2P(OR_f)_3$ 5, R = CH_3; 6, R = C_6H_5

$R_f = CH(CF_3)_2$

variable-temperature ^1H NMR spectra showed that intramolecular ligand reorganization could be slowed on the NMR time scale. More recently Schmutzler and his coworkers[4] have prepared a number of phosphoranes containing hexafluoroisopropoxy groups ($OCH(CF_3)_2 = OR_f$). Compounds 2–5 are examples. Variable-temperature ^{19}F NMR measurements were reported for compounds 3 and 5. Compound 3 showed two different hexafluoroisopropoxy groups below 30 °C. Given the chemical shift differences and the reported coalescence temperatures, one can calculate $\Delta G^\ddagger = 15$ kcal/mol for the process that renders the groups equivalent. Compound 5 had nonequivalent hexafluoroisopropoxy groups up to 60 °C; once again $\Delta G^\ddagger = 16$ kcal/mol can be calculated. The fact that 3 shows such a high $\Delta G^\ddagger$ is surprising, and Schmutzler et al. concluded that steric effects are probably responsible for the high activation energy.

It was the purpose of this work to investigate the reactions of hexafluoroisopropyl benzenesulfenate (7) with a variety of trivalent phosphorus compounds. It was hoped that the results of this investigation would provide information on the nature of these reactions and also on the properties of phosphoranes that might result therefrom.

Results and Discussion

The benzenesulfenate 7 can be prepared by reaction of benzenesulfenyl chloride with hexafluoroisopropyl alcohol in the presence of triethylamine. Unlike trifluoroethyl benzenesulfenate which is quite stable, compound 7 is quite unstable and decomposes at room temperature. It has been prepared and used without purification. Reaction of 7 with tris(1,1,1,3,3,3-hexafluoroisopropyl) phosphite (8) proceeded smoothly and yielded the phosphorane 9 (eq 1).

$$\underset{7}{C_6H_5SOCH(CF_3)_2} + \underset{8}{[(CF_3)_2CHO]_3P} \rightarrow \underset{9}{C_6H_5SP[OCH(CF_3)_2]_4} \quad (1)$$

It had been observed earlier in the trifluoroethoxy series that the analogue of 9 could be isolated and that it reacts further with another mole of sulfenate to provide pentakis(trifluoroethoxy)phosphorane. Compound 9 did not react with another mole of 7 under a variety of conditions, and thus compound 2 cannot be obtained by this sequence. Compounds 10 and 11 were allowed to react with 2 mol of 7 (eq 2) to afford 4 and 6. Triphenylphosphine (12) was

$$\underset{\substack{10,\ n=1\\ 11,\ n=2}}{(C_6H_5)_nP[OCH(CF_3)_2]_{3-n}} + 7 \rightarrow \underset{\substack{4,\ n=1\\ 6,\ n=2}}{(C_6H_5)_nP[OCH(CF_3)_2]_{5-n}} \quad (2)$$

also allowed to react with 7; triphenylphosphine oxide was formed as the sole phosphorus-containing product.

† Dedicated to Professor W. von E. Doering on the occasion of his 65th birthday.

(1) Denney, D. B.; Denney, D. Z.; Hammond, P. J.; Wang, Y. *J. Am. Chem. Soc.* **1981**, *103*, 1785.

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(3) Szele, I.; Kubisen, S. J., Jr.; Westheimer, F. J. *J. Am. Chem. Soc.* **1976**, *98*, 3533.

(4) (a) Dakternieks, D.; Roschenthaler, G.-V.; Schmutzler, R. *J. Fluorine Chem.* **1978**, *12*, 413. (b) Dakternieks, D.; Roschenthaler, G. V.; Schmutzler, R. *Ibid.* **1978**, *11*, 387.

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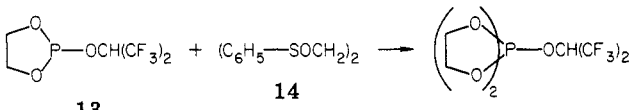
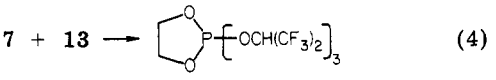
The phosphorane **15** was obtained from the reaction of **13** and **14** (eq 3). Similarly, **16** was obtained from the



13 **14** **15** (3)

reaction of **7** and **13** (eq 4). Compounds analogous to **15** and **16** have been prepared from the trifluoroethyl benzenesulfenate.

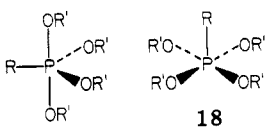


16 (4)

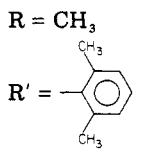
In general, the reactions of **7** have led to phosphoranes. It seems that triphenylphosphine did indeed react to give bis(1,1,1,3,3,3-hexafluoroisoproxy)triphenylphosphorane but that this material is too unstable to be isolated. This supposition is based on the fact that diphenyl disulfide was formed as the other product of the reaction.

The variable-temperature ^{19}F NMR spectra of **9** show that at room temperature all of the fluorines are equivalent. When a sample is cooled, two resonances for different kinds of fluorines are found. Coalescence was found at −26 °C and $\Delta G^{\ddagger}$ = 12 kcal/mol for the process that renders the fluorines equivalent. The most reasonable explanation for these spectra is that **9** undergoes Berry pseudorotation and that below −26 °C this process is slow on the ^{19}F NMR time scale (see Tables I and II for NMR data).

In the case of the Westheimer experiment it was not possible to distinguish between the trigonal-bipyramidal (TBP) structure **17** and the square-pyramidal (SP)



17 **18**



structure **18**. In order for the structure to be **18**, it was necessary to postulate that there was restricted rotation about the P–O bonds which was deemed unlikely. A similar situation arises with **9**. In this case a structure analogous to **17** is highly favored. If it is a SP analogous to **18**, then pairs of trifluoromethyl groups bonded to the same carbon become nonequivalent. This situation should lead to F–C–C–C–F coupling, usually ca. 8 Hz,[5] and no such coupling was observed. The structure analogous to **17** is by far the most likely. The trifluoroethoxy analogue of **9** showed only broadening of the ^{19}F NMR resonance at −97 °C. It seems likely that the barrier to intramolecular ligand reorganization is somewhat less for this compound than it is for **9**. It is possible, of course, that the chemical shift difference for apical and equatorial trifluoroethoxy groups is zero.

The variable-temperature ^{19}F NMR spectrum of **2**, prepared by the method of Schmutzler et al.,[4b] showed broadening at −95 °C. No separation into different resonances was observed. It is possible that intramolecular ligand reorganization is being slowed. It is interesting to note that it appears that no acyclic pentaalkoxyphosphorane has ever had its intramolecular ligand reorganization slowed sufficiently so that separate equatorial and apical groups have been observed. The most likely candidate, pentakis(perfluoro-*tert*-butoxy)phosphorane, has been prepared,[6] but no variable-temperature NMR studies have been reported.

The variable-temperature ^{19}F NMR spectra of **4** showed that at room temperature all of the fluorines are equivalent. Coalescence occurred at −10 °C, and below that temperature two separate resonances for nonequivalent fluorines were found. The $\Delta G^{\ddagger}$ for the process that renders them equivalent is 13 kcal/mol. These results are in total agreement with those reported by Schmutzler et al. for compound **3**. The origin of this barrier is of considerable interest. The Berry mechanism for pseudorotation has as the lowest energy path one in which the phenyl group remains in an equatorial position while the two apical and two equatorial groups exchange positions via an SP transition state. A similar process explains the interconversion of the groups of **2**. This process appears to have a relatively low barrier to interconversion. In fact, compounds **3** and **4** represent, other than **1**, the only documented cases of significant barriers to pseudorotation in monoaryl or monoalkyl tetrafluoro or tetraalkoxyphosphoranes. This uniqueness has been further substantiated by preparing tetraisopropoxyphenylphosphorane. The variable-temperature ^{13}C NMR spectra of this material showed no change from room temperature to −75 °C. A similar result was obtained for the pentaisopropoxyphosphorane.[7] Although a methyl group is somewhat smaller than a trifluoromethyl group (the van der Waals radii are 1.2 Å for C–H and 1.35 Å for C–F),[8] it does not seem reasonable to attribute the rather large barrier found for **3** and **4** to steric effects alone. The other factor is an increase in repulsions of nonbonded electrons as the SP transition state is approached. An inspection of a model of **4** indicates that the four hexafluoroisopropoxy groups are closer in the SP state than in the TBP. In the case of **2** there appears to be little difference in the proximity of the groups in either the SP or TBP structures, and thus the low barrier to ligand reorganization can be understood as a destabilization of the TBP structure of **2**.

The variable-temperature ^{19}F NMR spectra of **6** showed a coalescence at 30 °C which led to two different resonances for trifluoromethyl groups in the ratio of 2:1; the $\Delta G^{\ddagger}$ for the process is 16 kcal/mol. This observation is expected, and it is most easily explained by a TBP structure in which the two phenyl groups and an hexafluoroisopropoxy group occupy the three equatorial positions. For comparison's sake the $\Delta G^{\ddagger}$ for the trifluoroethoxy analogue was found to be 14 kcal/mol.

At −60 °C three resonances in the ratio 1:1:1 were found. Two of them were doublets with J_{HCCF} = 4.6 Hz and J_{HCCF} = 5.1 Hz; the other resonance was more complicated. This is probably due to long-range coupling of the phosphorus to the fluorines of the equatorially situated hexafluoroisopropoxy group. If the original premise is correct, i.e., that the TBP no longer undergoes pseudorotation, then the further splitting can only be due to nonequivalence of the three hexafluoroisopropoxy groups. This means that the two apical groups have become nonequivalent. This

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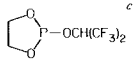
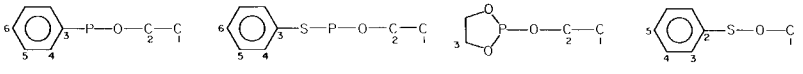
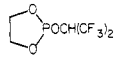
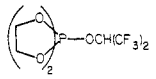
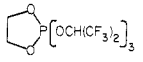
Table I. ^{13}C NMR Data[a,b]

compd	chemical shift, ppm (J, Hz)					
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
$(C_6H_5)_2P[OCH(CF_3)_2]$[c] (11)	122.2 (q, J_{CF} = 288.0)	77.4 (dh,[f] J_{CCF} = 33.1, J_{COP} = 24.9)	140.1 (d, J_{CP} = 15.1)	131.3 (d, J_{CCP} = 22.7)	129.1 (d, J_{CCCP} = 7.4)	130.9 (s)
$C_6H_5P[OCH(CF_3)_2]_2$[d] (10)	121.3 (q, J_{CF} = 287.5)	74.1 (m, J_{CCF} = 34.2)	136.5 (d, J_{CP} = 13.3)	131.8 (d, J_{CCP} = 44.3)	129.2 (d, J_{CCCP} = 7.9)	129.4 (s)
$P[OCH(CF_3)_2]_3$[c] (8)	120.8 (q, J_{CF} = 282.5)	70.5 (dh, J_{CCF} = 35.7, J_{COP} = 8.5)				
$(C_6H_5)_2P[OCH(CF_3)_2]_3$[c,g] (6)	120.5 (q, J_{CF} = 270.0)	73.8 (m)				
$(C_6H_5)P[OCH(CF_3)_2]_4$[c] (4)	117.8 (q, J_{CF} = 283.0)	73.7 (dh, J_{CCF} = 35.6, J_{COP} = 12.3)	131.6 (d, J_{CP} = 242.0)	129.0 (d, J_{CCP} = 21.0)	128.1 (d, J_{CCCP} = 13.3)	132.5 (d, J_{CCCCP} = 4.4)
$P[OCH(CF_3)_2]_5$[e] (2)	117.1 (q, J_{CF} = 282.0)	71.2 (dh, J_{CCF} = 23.0, J_{COP} = 15.6)				
$C_6H_5SP[OCH(CF_3)_2]_4$[c] (9)	121.0 (dq, J_{CF} = 283.7, J_{CCOP} = 4.4)	74.7 (dh, J_{CCF} = 35.1, J_{COP} = 14.2)	130.8 (d, J_{CSP} = 6.0)	135.7 (d, J_{CCSP} = 8.5)	129.4 (s)	129.6 (s)
$Cl_2P[OCH(CF_3)_2]_3$[d] (19)	120.4 (dq, J_{CF} = 283.1, J_{CCOP} = 8.5)	75.1 (dh, J_{CCF} = 36.0, J_{COP} = 15.3)				
	122.5 (q, J_{CF} = 281.8)	70.1 (dh, J_{CCF} = 34.2, J_{COP} = 17.9)	65.2 (d, J_{COP} = 8.7			
$(C_6H_5SOCH_2)_2$[d] (14)	76.9	140.2	123.9	129.1	126.8	

[a] See Experimental for details of NMR experiments. [b] Numbering systems are as follows: 

[c] Solvent is $CDCl_3$. [d] Solvent is CD_2Cl_2. [e] Solvent is $CFCl_3$–CD_2Cl_2. [f] Doublet of heptets. [g] Aromatic region very complex.

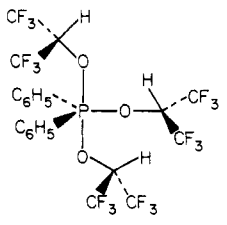
Table II. NMR Spectral Data[a,b]

compd	^{31}P	^{1}H		^{19}F temp, °C	^{19}F shift
$C_6H_5SOCH(CF_3)_2$ (7)		4.4 (h, 1 H, J_{HCCF} = 6.0)	7.6 (m,[c] 5 H)	26[c]	−80.21 (d, J_{FCCH} = 6.0)
$(C_6H_5)_2POCH(CF_3)_2$ (11)	142.0[c] (h, J_{POCCF} = 6.6)	4.6 (dh, 1 H, J_{HCOP} = 10.0, J_{HCCF} = 6.0)	7.5 (m,[c] 10 H)	26[c]	−79.99 (dd, J_{FCCH} = 6.4, J_{FCCOP} = 6.4)
$C_6H_5P[OCH(CF_3)_2]_2$ (10)	190.0[d] (m)	4.7 (dh, 2 H, J_{HCOP} = 9.0, J_{HCCF} = 5.0)	7.6 (m,[d] 5 H)	26[d]	−79.00 (d, J_{FCCH} = 5.2)
$P[OCH(CF_3)_2]_3$ (8)	141.0[c,g] (m)	4.5 (dh,[c,h] J_{HCOP} = 9.7, J_{HCCF} = 5.3)		26[c,i]	−80.68 (d, J_{FCCH} = 4.8)
$P[OCH(CF_3)_2]_5$ (2)	−88.1[f,g]	5.1 (m)[f,h]		−95[f]	broad absorption
				26[f,i]	−73.7 (s)
$(C_6H_5)_2P[OCH(CF_3)_2]_3$ (6)	−38.0[c]	3.7-4.6 (m, 3 H)	7.6 (m,[c] 10 H)	−60[c]	−72.76 (d, 6 F, J_{FCCH} = 4.6), −73.10 (m, 6 F), −73.60 (d, 6 F, J_{FCCH} = 5.1)
				−22[c]	−73.10 (m), −72 to −75 (br abs)
				26[c]	−73.22 (m)
				60[e]	−73.10 (d, J_{FCCH} = 5.1)
$C_6H_5P[OCH(CF_3)_2]_4$ (4)	−62.0[c]	4.8-5.5 (m, 4 H)	7.5 (m,[c] 5 H)	−20[c]	−77.1 (12 F), −77.9 (12 F)
				−3[c]	−74 to −78 (br abs)
				26[c]	−77.5
				85[e]	−78.9 (d, J_{FCCH} = 4.6)
$C_6H_5SP[OCH(CF_3)_2]_4$ (9)	−54.0[c] (m)	4.8-5.4 (m, 4 H)	7.1-7.6 (m,[c] 5 H)	−56[c]	−72.13 (12 F), −73.65 (12 F)
				−26[c]	broad absorption
				26[c]	−72.93 (d, J_{FCCH} = 2.9)
$Cl_2P[OCH(CF_3)_2]_3$ (19)	−56.3[d,g]	5.5 (dh,[c,h] J_{HCOP} = 20.0, J_{HCCP} = 5.0)		26[c,i]	−79.74 (d, J_{FCCH} = 4.6)
$(C_6H_5SOCH_2)_2$ (14)		3.9 (s, 4 H)	7.4 (m,[d] 10 H)		
 13	140.1[d] (h, J_{POCCF} = 6.7)	3.9-4.4 (m, 4 H)	4.4-4.9 (m,[c] 1 H)	26[d]	−81.0 (dd, J_{FCCH} = 6.5, J_{FCCOP} = 6.5)
 15	−29.7[d] (m)	3.7-4.2 (m, 8 H)	5.2-5.5 (m,[c] 1 H)	26[d]	−78.58 (br)
 16	−62.6[c] (m)	3.8-4.6 (m, 4 H)	4.7-5.5 (m,[c] 3 H)	26[c]	−76.95 (m)

[a] See Experimental for details of NMR experiments. The chemical shifts are in parts per million and the coupling constants in hertz. [b] An h indicates a heptet. [c] Solvent is $CDCl_3$. [d] Solvent is CD_2Cl_2. [e] Solvent is toluene-d_8. [f] Solvent is $CFCl_3$–CD_2Cl_2. [g] Reference 4b reports ^{31}P NMR shifts of 141 ppm for 8, −76 ppm for 19 and −84 ppm for 2. [h] Reference 4b reports ^{1}H NMR shifts of 4.8 ppm for 8, 5.9 ppm for 19 and −5.2 ppm for 2. [i] Reference 4b reports −76.0 ppm for 8, −77.3 ppm for 19 and −73 ppm for 2.

nonequivalence is not due to diastereotopic trifluoromethyl groups. If such had been formed, then F–C–C–C–F coupling would be observed.

An inspection of a model shows that there is a structure, **20**, in which three pairs of nonequivalent trifluoromethyl groups are present and in which they are quite far apart. If this is the correct structure, then restricted rotation about at least one apical P–O bond is required. These interesting observations deserve further scrutiny, and other molecules are currently under investigation.



20

As was mentioned earlier the trifluoroethoxy-containing phosphoranes often reacted with trifluoroethoxide ion to give hexacoordinated materials.

Treatment of **9** with 2 mol of 1,1,1,3,3,3-hexafluoroisopropoxide ion led after 30 min to 78% of **8** and 20% of **9** (eq 5). This reaction was not investigated in detail, and no other statement concerning it can be made at this time.

Compound **6** reacted with 1,1,1,3,3,3-hexafluoroisopropoxide ion to give a phosphoryl containing compound.

$$C_6H_5SP(OCH(CF_3)_2)_4 + 2(CF_3)_2CHO^- \rightarrow \underset{9}{} \quad \underset{8}{P(OCH(CF_3)_2)_3} \quad (5)$$

No evidence for an hexacoordinated material could be obtained.

Reaction of **16** with 1,1,1,3,3,3-hexafluoroisopropoxide ion gave a compound with δ −109 along with a phosphoryl compound with δ 0.75. The compound with δ −109 may well be a hexacoordinated material. Similarly, **15** reacted to give a mixture of phosphoryl-containing compounds as well as a resonance at δ −87 which also may be due to a hexacoordinated material. The main conclusion from these limited investigations is that P(VI) compounds containing 1,1,1,3,3,3-hexafluoroisopropoxy groups are very unstable.

Experimental Section

^{1}H NMR spectra were recorded with Varian Model T-60 and A-60A spectrometers. Chemical shift values are reported in parts per million relative to internal tetramethylsilane. ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded with a Varian Model FT-80 spectrometer equipped with a variable-temperature broad-band probe. In all cases nuclei which are deshielded relative to their respective standard are assigned a positive chemical shift. ^{13}C NMR spectra were obtained by using full proton decoupling, a 45° flip angle, and a 2-s repetition rate with no pulse delay. All ^{13}C chemical shifts are reported in parts per million relative to internal tetramethylsilane. ^{19}F NMR spectra were acquired by using a 45° flip angle, a 2-s repetition rate with no pulse delay, and full proton coupling. Chemical shifts are reported relative to external trichlorofluoromethane. ^{31}P NMR spectra were acquired by using a 45° flip angle, a 1-s repetition rate with no pulse delay, and full proton decoupling. Chemical shifts are reported relative to external phosphoric acid (85%).

All reactions and as many manipulations as possible were carried out in a nitrogen atmosphere. All solvents were scrupulously dried and freshly distilled.

Preparation of 1,1,1,3,3,3-Hexafluoro-2-propyl Benzenesulfenate (7). To a solution of 1,1,1,3,3,3-hexafluoro-2-propanol (3.36 g, 0.02 mol) and triethylamine (2.02 g, 0.02 mol) in petroleum ether (bp 35–60 °C, 40 mL) at −40 °C was added, with stirring, benzenesulfenyl chloride (2.89 g, 0.02 mol). The reaction mixture was allowed to warm to room temperature, and it was stirred for an additional hour. The solid was removed by filtration, and the filtrate was concentrated at reduced pressure. The residual oil was molecularly distilled [T_{block} = 58 °C (0.25 mm)] to yield 3 g (54%) of **7**. This material decomposed at room temperature but could be stored in solution at −10 °C.

Preparation of 1,1,1,3,3,3-Hexafluoro-2-propyl Diphenylphosphinite (11). To a stirred solution of diphenylphosphinous chloride (11.03 g, 0.05 mol) and triethylamine (5.05 g, 0.05 mol) in ether (100 mL) at −40 °C was added, with stirring, 1,1,1,3,3,3-hexafluoro-2-propanol (8.4 g, 0.05 mol). The reaction mixture was allowed to warm to room temperature, and it was stirred for an additional hour. After removal of the solid by filtration, the filtrate was concentrated at reduced pressure. The residual oil was distilled (93 °C, 0.7 mm) to yield 11.5 g (65%) of **11**. Anal. Calcd for $C_{15}H_{11}OF_6P$: C, 51.15; H, 3.15. Found: C, 51.41; H, 3.23.

Preparation of Diphenyltris(1,1,1,3,3,3-hexafluoro-2-propoxy)phosphorane (6). To a stirred solution of 1,1,1,3,3,3-hexafluoro-2-propyl benzenesulfenate (1.66 g, 0.006 mol) in pentane (10 mL) at −70 °C was added the phosphinite **11** (1.06 g, 0.003 mol). The reaction mixture was allowed to warm to room temperature, and it was then stirred for an additional h. The reaction mixture was cooled to −40 °C and the solid was removed by filtration. The filtrate was concentrated at reduced pressure to yield a solid. This material was sublimed (52 °C, 0.025 mm) to yield 1.5 g (74.8%) of **6**. Anal. Calcd for $C_{21}H_{13}O_3F_{18}P$: C, 36.73; H, 1.89. Found: C, 36.63; H, 1.93.

Reaction of Triphenylphosphine (12) with 1,1,1,3,3,3-Hexafluoro-2-propyl Benzenesulfenate (7). To a stirred solution of **7** (3.0 g, 0.011 mol) in petroleum ether (bp 35–60 °C, 25 mL) at −78 °C was added triphenylphosphine (1.43 g, 0.0054 mol) in dichloromethane (10 mL). The reaction mixture was allowed to warm to room temperature, and it was stirred for 2 h. The mixture was then cooled to −60 °C, and it was filtered. The precipitate could be recrystallized to yield a solid which was identical in all respects with diphenyl disulfide. The filtrate was concentrated to yield a solid which was recrystallized from petroleum ether (bp 35–60 °C). This material (mp 156 °C) was identical in all respects with triphenylphosphine oxide.

Preparation of Tris(1,1,1,3,3,3-hexafluoro-2-propyl) Phosphite (8). To a stirred solution of phosphorus trichloride (8.25 g, 0.06 mol) and triethylamine (19.2 g, 0.19 mol) in tetrahydrofuran at −20 °C was added 1,1,1,3,3,3-hexafluoro-2-propanol (31.9 g, 0.19 mol). The reaction mixture was allowed to warm to room temperature. The solid was removed by filtration, and the filtrate was concentrated at reduced pressure. The residual oil was distilled at 87 °C (47 mm) [lit.[4b] 130 °C (760 mm)].

Preparation of Tetrakis(1,1,1,3,3,3-hexafluoroisopropoxy)(phenylthio)phosphorane (9). To a stirred solution of 1,1,1,3,3,3-hexafluoro-2-propanol (2.52 g, 0.015 mol) and triethylamine (1.52 g, 0.015 mol) in pentane (25 mL) at −30 °C was added benzenesulfenyl chloride (2.16 g, 0.015 mol). After having warmed to room temperature, the reaction mixture was stirred for 1 h. The solid was removed by filtration. The filtrate was added slowly to a stirred solution of the phosphite **8** (3.19 g, 0.006 mol) in pentane (10 mL) which had been cooled to −78 °C. After the addition was completed, the reaction mixture was allowed to warm to room temperature. It was stirred for another hour. After removal of the solvent at reduced pressure, there remained a white solid. This could be purified by sublimation (45 °C, 0.025 mm) to yield 3.2 g (66%) of **9**, mp 61 °C. Anal. Calcd for $C_{18}H_9O_4F_{24}PS$: C, 26.75; H, 1.12. Found: C, 26.89; H, 1.33.

Preparation of Dichlorotris(1,1,1,3,3,3-hexafluoro-2-propoxy)phosphorane (19). Chlorine (0.65 g, 0.009 mol) was bubbled into a tube, at −78 °C, containing **8** (4.86 g, 0.009 mol). The reaction mixture was allowed to return to room temperature very slowly. The product was distilled at 28–30 °C (0.025 mm) [lit.[4b] 48 °C (0.01 mm)] to yield 4.5 g (83%) of **19**.

Preparation of Pentakis(1,1,1,3,3,3-hexafluoropropoxy)-phosphorane (2). This material was synthesized by the method of Schmutzler et al.[4b]

Preparation of Bis(1,1,1,3,3,3-hexafluoropropyl) Phenylphosphonite (10). To a stirred solution of phenylphosphonous dichloride (3.58 g, 0.02 mol) in ether (20 mL) at −40 °C were added 1,1,1,3,3,3-hexafluoro-2-propanol (6.72 g, 0.04 mol) and triethylamine (4.04 g, 0.04 mol). The reaction mixture was allowed to warm to room temperature, and it was stirred for an additional 2 h. The solid which formed was removed by filtration, and the filtrate was concentrated at reduced pressure. The residual oil was distilled [58–59 °C (0.01 mm)] to yield 7.1 g (80.3%) of product **10**.

Preparation of Tetrakis(1,1,1,3,3,3-hexafluoropropoxy)-phenylphosphorane (4). To a stirred solution of 1,1,1,3,3,3-hexafluoro-2-propanol (2.0 g, 0.012 mol) and triethylamine (1.21 g, 0.012 mol) in pentane (20 mL) at −20 °C was added benzenesulfenyl chloride (1.73 g, 0.012 mol). The reaction mixture was allowed to warm to room temperature slowly. The solid was removed by filtration. The filtrate was cooled to −40 °C, and to this was added, with stirring, the phosphonite **10** (1.33 g, 0.003 mol). The reaction mixture was allowed to warm to room temperature. Stirring was continued for 1 h. The reaction mixture was again cooled to −40 °C, and the solid was removed by filtration. The filtrate was concentrated at reduced pressure. The residue was sublimed (75 °C, 0.05 mm) to yield 1.8 g (77.3%) of a white solid, mp 75–77 °C.

Preparation of 1,1,1,3,3,3-Hexafluoro-2-propyl 1,2-Ethanediyl Phosphite (13). To a stirred solution of ethylene glycol (6.2 g, 0.1 mol) and pyridine (15.8 g, 0.2 mol) in ether (150 mL) at −30 °C was added phosphorus trichloride (13.7 g, 0.1 mol) in ether (30 mL). After the mixture had been stirred for 1 h, the solid was removed by filtration. To the filtrate at −30 °C were added 1,1,1,3,3,3-hexafluoro-2-propanol (16.8 g, 0.1 mol) and pyridine (7.9 g, 0.1 mol) in ether (20 mL). The reaction mixture was allowed to warm to room temperature, and it was stirred for an additional 1 h. The solid was removed by filtration, and the filtrate was concentrated at reduced pressure. The residual oil was distilled [30 °C (1.5 mm)] to yield 6.2 g (24%) of **13**.

Reaction of Benzenesulfenyl Chloride with Ethylene Glycol. To the stirred solution of benzenesulfenyl chloride (7.25 g, 0.05 mol) in tetrahydrofuran (50 mL) at −40 °C was added ethylene glycol (1.55 g, 0.025 mol) and triethylamine (5.02 g, 0.05 mol). The reaction mixture was allowed to warm to room temperature, and it was stirred for an additional 2 h. The solid was removed by filtration, and the filtrate was concentrated at reduced pressure. The residual oil was molecularly distilled [T_{block} = 70 °C (0.25 mm)] to yield **14**. Anal. Calcd for $C_{14}H_{14}O_2S_2$: C, 60.43; H, 5.03. Found: C, 60.81; H, 4.85.

Preparation of 16. To a stirred solution of 1,1,1,3,3,3-hexafluoro-2-propanol (2.69 g, 0.016 mol) and triethylamine (1.62 g, 0.016 mol) in pentane (25 mL) at −30 °C was added benzenesulfenyl chloride (2.31 g, 0.016 mol). The reaction mixture was allowed to warm to room temperature, and it was then stirred for an additional 1 h. The solid was removed by filtration. To the filtrate at −75 °C was added **13** (1.032 g, 0.004 mol) in pentane (10 mL). The reaction mixture was allowed to warm to room temperature, and it was stirred for an additional 1 h. The mixture was cooled to −20 °C, and it was filtered. The filtrate was concentrated at reduced pressure, and the residual oil was molecularly distilled [T_{block} = 50° (0.01 mm)] to yield 1.0 g (42%) of product **16**.

Preparation of 15. To a stirred solution of 1,2-ethanediyl bis[benzenesulfenate] (**14**; 2.17 g, 0.0078 mol) in pentane (20 mL) and tetrahydrofuran (5 mL) at −70 °C was added **13** (2.01 g, 0.0078 mol). The reaction mixture was allowed to warm to room temperature and it was stirred for an additional 1 h. The reaction mixture was concentrated at reduced pressure and the residual solid was sublimed (50 °C, 0.05 mm).

Reaction of 6 with Potassium 1,1,1,3,3,3-Hexafluoroisopropoxide. To a stirred solution of **6** (0.7 g, 0.001 mol) in toluene (1 mL), at 10 °C was added a solution of potassium 1,1,1,3,3,3-hexafluoroisopropoxide (0.4 g, 0.002 mol) and 18-crown-6 ether (0.53 g, 0.002 mol) in toluene (1 mL). The reaction mixture was allowed to warm to room temperature. The ^{31}P NMR spectrum of this solution showed only one absorption at δ 27.5 (external lock).

Reaction of 15 with Potassium 1,1,1,3,3,3-Hexafluoroisopropoxide. To a stirred solution of **15** (0.25 g, 0.0008 mol) in benzene-d_6 was added potassium 1,1,1,3,3,3-hexafluoroisopropoxide (0.32 g, 0.0016 mol) and 18-crown-6 ether (0.42 g, 0.0016 mol) in benzene-d_6 (2 mL). After the mixture was stirred at room temperature for 30 min, the ^{31}P NMR spectrum of the reaction mixture showed resonances at δ −86.7, −1.5, −1.0, −0.9, −0.2 (C_6D_6).

Reaction of 16 with Potassium 1,1,1,3,3,3-Hexafluoroisopropoxide. To a stirred solution of **16** (1.0 g, 0.0017 mol) at 10 °C were added potassium 1,1,1,3,3,3-hexafluoroisopropoxide (0.7 g, 0.0034 mol) and 18-crown-6 ether (0.89 g, 0.0034 mol) in benzene-d_6 (1.5 mL). The reaction mixture was allowed to warm to room temperature. The ^{31}P NMR spectrum of the reaction mixture showed two absorptions at δ −109.5 and 0.8 (C_6D_6).

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Riccardin A and Riccardin B, Two Novel Cyclic Bis(bibenzyls) Possessing Cytotoxicity from the Liverwort *Riccardia multifida* (L.) S. Gray

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Riccardin A (**1**) and riccardin B (**4a**), two novel cyclic bis(bibenzyls) possessing cytotoxic activity, were isolated from the liverwort *Riccardia multifida* (L.) S. Gray together with 6-(3-methyl-2-butenyl)indole (**9**). Proof for the proposed structure and definite evidence for the stereochemistry of **1** were provided by X-ray analysis of the acetate of **1**. The structure of **4a** was suggested by the analysis of 400-MHz ^1H NMR spectral data.

Some liverworts contain potent allergenic, cytotoxic, and antifeedant sesquiterpenoids.[1] On the other hand, various prenylbibenzyls[2,3] and prenyl benzoates[4] have been isolated from a few liverworts belonging to the Jungermanniales. In our continuing search of biologically active substances of the liverworts, we investigated the chemical constituents of *Riccardia multifida* (L.) S. Gray, belonging to the Metzgeriales, and isolated two structurally unique cyclic bis(bibenzyl) derivatives, named riccardin A (**1**) and B (**4a**) (Chart I), which possessed cytotoxic activity vs. KB cells.

Silica gel chromatography of the ether extract of the ground material resulted in the isolation of **1** (8% of the total extract) and **4a** (7%), together with the previously known 6-(3-methyl-2-butenyl) indole (**9**, 8%).[5]

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