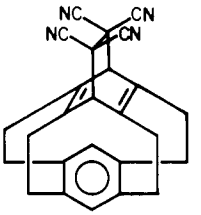
chloride under nitrogen with stirring at room temperature. The solution became a reddish brown and was stirred at room temperature for 3 days. A saturated, aqueous solution of sodium bicarbonate was added, and the organic layer was extracted with chloroform. The chloroform layer was washed with water, dried, and concentrated. The residual solid was purified by preparative thin-layer chromatography over silica gel using chloroform as eluant to give 37 mg of pale, yellow crystals. Recrystallization of these from chloroform then gave 35 mg (40%) of *50* as white prisms; mp 220 °C dec; UV ($CHCl_3$) λ_{max} 297 nm (ϵ 223); ^1H NMR δ 1.75–3.26 (m, CH_2 and CH); mass spectrum, *m/e* 502, 500, 464, 386, 312. Anal ($C_{32}H_{25}N_4Cl$) C, H, N.

Structure **50** for this substance has been established by an X-ray crystallographic analysis.[43]

Diels–Alder Addition of Tetracyanoethylene to [2₄](1,2,4,5)Cyclophane To Give 51. Addition of tetracyanoethylene (19 mg) at room temperature to a solution of 10 mg of [2₄](1,2,4,5)cyclophane[8b] in 20 mL of chloroform led to an immediate deep blue color. The color disappeared in a few seconds and white crystals separated from the solution. These



51

were collected by filtration and dried to give 12 mg (100%) of **51** as white crystals: mp >215 °C dec; ^1H NMR δ 2.20–3.12 (16 H, m, CH_2), 360 (2 H, s, CH), 6.76 (2 H, s, ArH); mass spectrum, *m/e* 260 (M^+ – TCNE), 245, 128. Anal. ($C_{26}H_{20}N_4$) C, H, N.

Acknowledgment. We thank the National Science Foundation for their support of this investigation.

Preparation and Chemistry of Penta- and Hexacoordinated Phosphorus Compounds Containing Trifluoroethoxy Groups

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Abstract: Tris(trifluoroethyl) phosphite, bis(trifluoroethyl) phenylphosphonite, trifluoroethyl diphenylphosphinite, and triphenylphosphine all react with 2 mol of trifluoroethyl benzenesulfenate to give pentacoordinated phosphorus compounds in which two trifluoroethoxy groups have been added to the original tricoordinated phosphorus compound. When tris(trifluoroethyl) phosphite was allowed to react with 1 mol of trifluoroethyl benzenesulfenate, tetrakis(trifluoroethyl)thiophenylphosphorane was isolated. When the other tricoordinated phosphorus compounds were allowed to react with 1 mol of trifluoroethyl benzenesulfenate, only recovered starting material and the pentacoordinated phosphorus compounds formed by the addition of two trifluoroethoxy groups were found in the reaction mixtures. All of the trifluoroethoxy-containing phosphoranes except for bis(trifluoroethoxy)triphenylphosphorane reacted with trifluoroethoxide ion to give hexacoordinated phosphorus compounds. Tris(trifluoroethoxy)diphenylphosphorane reacts with trifluoroethoxide ion to give the hexacoordinated compound in which the phenyl groups are cis to each other. This material rapidly isomerizes to a mixture of trans (82%) and cis (18%). Treatment of pentakis(trifluoroethoxy)phosphorane with 1 and 2 mol of ethylene glycol yielded new phosphoranes containing one and two five-membered rings, respectively. Both reacted with trifluoroethoxide ion to give hexacoordinated phosphorus compounds. In the case of the compound containing two five-membered rings, both cis and trans isomers were detected in the ratio of 2:1 at equilibrium.

The chemistry of pentacoordinated phosphorus compounds has received much attention during the last two decades, and many important questions concerning these molecules have been answered.[1] There remain several areas of interest within the chemistry of these substances. In particular, an understanding of steric effects in governing stability and structure remains to be delineated. The factors which govern intermolecular and intramolecular ligand reorganization reactions have received much attention. Attempts to generalize rules purported to govern these processes have met with some success, but important exceptions have been noted. The strutures of these materials in the crystalline state have been shown to vary from trigonal bipyramidal (TBP) to square or rectangular pyramidal (SP or RP).[2] Interestingly, the structures of many of these substances in solution are not known. Considerable effort has been expended in developing an apicophilicity series, i.e., within a TBP which ligands will prefer the apical positions, and certainly progress has been made in this area. Most of these studies have involved phosphoranes with halogen, oxygen, and to a lesser degree carbon and nitrogen bonded to phosphorus, and thus there is potentially a vast unknown area for further exploration.

The chemistry of hexacoordinated phosphorus compounds has received much less attention than that of the pentacoordinated materials. Muetterties and Mahler[3] showed that electronegative elements, in particular fluorine, stabilize the hexacoordinated state. Somewhat later Ramirez[4] and others suggested that hexacoordinated phosphorus compounds are formed during nucleophilic displacement reactions on pentacoordinated phosphorus com-

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(3) Muetterties, E. L.; Mahler, W. *Inorg. Chem.* **1965**, *4*, 119.

(4) (a) Ramirez, F.; Tasaka, K.; Desac, N. B.; Smith, C. P. *J. Am. Chem. Soc.* **1968**, *90*, 751. (b) Ramirez, F.; Loewengart, G. V.; Tsolis, E. A.; Tasaka, K. *Ibid.*, **1972**, *94*, 3531. (c) Ramirez, F.; Tasaka, K.; Hershberg, R. *Phosphorus* **1972**, *2*, 41. (d) Ramirez, F.; Lee, S.; Stern, P.; Ugi, I.; Gillespie, P. *Ibid.* **1974**, *4*, 21. (e) Chang, B. C.; Conrad, W. E.; Denney, D. B.; Denney, D. Z.; Edelman, R.; Powell, R. L.; White, D. W. *J. Am. Chem. Soc.* **1971**, *93*, 4004. (f) Archie, W. C.; Westheimer, F. H. *Ibid.* **1973**, *95*, 5955. (g) Aksnes, G. *Phosphorus and Sulfur* **1977**, *3*, 227.

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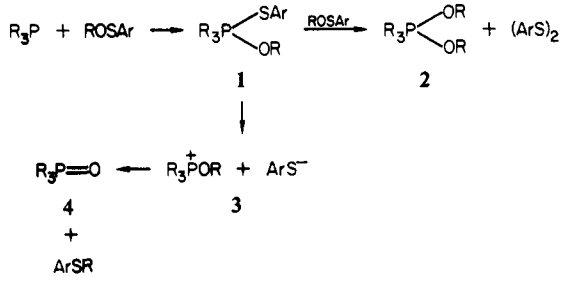
pounds. More recently hexaphenoxyphosphate,[5] hexamethoxyphosphate, and hexaethoxyphosphate[6] have been prepared in solution.

In another recent development, the stereochemistries of a number of hexacoordinated phosphates containing two five-membered rings with oxygen bonded to phosphorus and two other oxyligands or fluorine have been investigated. The crystal structure of one of these substances shows that the nonring ligands are cis to each other.[7] In another investigation, it was shown in several cases that addition of the nucleophile to bicyclic phosphoranes containing two five-membered rings with oxygen bonded to phosphorus yielded the trans products initially and that these materials subsequently isomerized to the cis compounds.[8] These findings are indicative of a potentially rich chemistry of hexacoordinated phosphorus compounds.

Several years ago it was reported that alkyl benzenesulfenates often react with tricoordinated phosphorus compounds to give pentacoordinated phosphorus compounds.[9] This reaction sequence is probably the most general for the production of oxyphosphoranes. The first step involves formation of a mixed oxythiophosphorane (**1**) which subsequently reacts with another mole



of alkyl benzenesulfonate to give **2**. The major side reaction is decomposition of **1** via the ion pair **3** to the phosphoryl compound **4** and an alkyl phenyl thioether. It was the purpose of this research to study the reactions of trifluoroethyl benzenesulfenate (**5**) with various trivalent phosphorus compounds. The products of these reactions have been investigated in a number of ways. In particular, ligand reorganization reactions have been investigated as have the conversion of the phosphoranes into hexacoordinated phosphorus compounds. The trifluoroethyl group was selected because it would stabilize the P(V) and P(VI) compounds as compared to nonfluorinated materials, and also the structures of the products could be probed by ^{19}F NMR. The sensitivity of ^{19}F NMR and the large chemical shift differences make it ideal for studying dynamic processes.

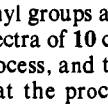
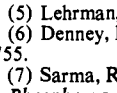
Results and Discussion

Compound **5** can be synthesized by conventional techniques, and it is readily handled. Reaction of **5** (2 mol) with the trivalent phosphorus compounds **6–9** yielded in all cases phosphoranes **11–14**. These materials are reasonably stable, and they can be obtained in pure form. Pertinent NMR data and analytical figures are collected in Table I.

Reaction of **5** (1 mol) with **6** led to the production of the thiooxyphosphorane **10**. Addition of another mole yielded the phosphorane **11**. When **5** (1 mol) was allowed to react with **7**, **8**, and **9** (1 mol), only the phosphoranes **12**, **13**, and **14** and unreacted starting material were found in the reaction mixtures.

The ^{19}F NMR spectrum of **10** shows that all of the trifluoroethyl groups are equivalent. The variable-temperature ^{19}F NMR spectra of **10** clearly show that the equivalence is due to a dynamic process, and the observation of POCH and PSC coupling shows that the process is intramolecular. At −97 °C the ^{19}F NMR

Table I. NMR Parameters and Analytical Data

compd	$^{31}P^a$	$^{19}F^a$	$^1H^{a,b}$	$^{13}C^{a,c}$	calcd C	calcd H	found C	found H
$C_6H_5SOCH_2CF_3$ (5)		−80.7, t (8.5)	4.05, q (8.5), 7.42, s	74.2, q (34.2); 132.2, q (278.7)	46.15	3.39	45.93	3.29
$P(OCH_2CF_3)_3$ (6)	139.3, q (4.5)	−82.3, dt (4.5, 8.2)	4.24, dq (8.2, 8.2)	60.8, dq (10.7, 37.2); 123.8, dq (6.2, 270.0)				
$C_6H_5P(OCH_2CF_3)_2$ (7)	167.2, q (3.5)	−81.5, dt (3.4, 8.5)	4.20, m; 7.10, m	64.0, dq (9.3, 36.0); 123.0, dq (6.1, 260.0)	39.23	2.96	39.72	2.93
$(C_6H_5)_2P(OCH_2CF_3)$ (8)	126.5, q (6.0)	−80.9, dt (6.0, 8.0)	4.06, dq (8.0, 8.0); 7.30, m	67.1, dq (22.0, 35.0); 122.0 dq (8.1, 270.0)	59.16	4.26	58.99	4.19
$(C_6H_5S)P(OCH_2CF_3)_4$ (10)	−50.6, s	−81.7, t (8.2)	4.18, dq (8.2, 8.2); 7.48, m	65.4, dq (11.4, 36.1); 124.2 dq (11.9, 280.1); 136.7,[d] d (6.9)	31.36	2.44	31.65	2.55
$P(OCH_2CF_3)_5$ (11)	−76.6, s	−82.3, t (8.3)	4.27, dq (8.3, 8.3)	65.5, dq (10.8, 36.3); 123.7, dq (13.0, 277.2)	22.83	1.92	23.02	2.04
$(C_6H_5)P(OCH_2CF_3)_4$ (12)	−61.7, s	−82.1, t (8.5)	4.08, dq (5.0, 8.5)	64.4, dq (8.8, 35.8); 123.7, dq (6.5, 267.5)	33.34	2.60	33.60	2.80
$(C_6H_5)_2P(OCH_2CF_3)_3$ (13)	−45.2, s	−80.7, mound	3.80, mound; 7.70, m	62.8, mound; 123.0, dq (11.2, 260.0)	44.83	3.34	44.95	3.40
$(C_6H_5)_3P(OCH_2CF_3)_2$ (14)	−58.5, s	−80.3, t (8.9)	2.94, dq (4.6, 8.9); 7.50, m	60.7, dq (6.1, 34.2); 124.3, dq (7.3, 278.0)				
 (15)	−52.5, s	−81.9, t (8.5)	4.32, dq (8.5, 8.5); 3.97, d (15)	60.6, d (2.7); 64.4, dq (9.6, 36.1); 123.3, dq (12.3, 277.7)	24.76	2.60	24.66	2.73
 (16)	−28.5	−82.0, dt (0.4, 8.6)	3.80, s; 4.03, s; 4.34 dq (8.6, 8.6)	59.9, d (4.9); 63.7, dq (7.9, 36.1); 123.0, dq (11.5, 268.5)	28.81	4.03	28.85	4.01

[a] The solvent is $CDCl_3$ and the temperature 30 °C. The numbers in parentheses are the coupling constants in Hz. [b] Integrations of respective areas are correct to ±5%. [c] The chemical shifts of the aromatic carbons are not listed unless relevant. [d] Ipso carbon.

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(6) Denney, D. B.; Denney, D. Z.; Ling, C. *J. Am. Chem. Soc.* **1976**, *98*, 6755.
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$CF_3CH_2OSC_6H_5$ + $R_1P(R_2)(R_3)$ ⟶

5

6, $R_1 = R_2 = R_3 = CF_3CH_2O$
7, $R_1 = R_2 = CF_3CH_2O$; $R_3 = C_6H_5$
8, $R_1 = CF_3CH_2O$; $R_2 = R_3 = C_6H_5$
9, $R_1 = R_2 = R_3 = C_6H_5$

$C_6H_5SP(R_1)(R_2)(R_3)$ (5 ⟶)
|
OCH_2CF_3

10, $R_1 = R_2 = R_3 = CF_3CH_2O$

$(CF_3CH_2O)_2P(R_1)(R_2)(R_3)$

11, $R_1 = R_2 = R_3 = CF_3CH_2O$
12, $R_1 = R_2 = CF_3CH_2O$; $R_3 = C_6H_5$
13, $R_1 = CF_3CH_2O$; $R_2 = R_3 = C_6H_5$
14, $R_1 = R_2 = R_3 = C_6H_5$

spectrum degenerated into a broad featureless absorption. These results suggest that the ligand reorganization has been slowed or that the broadness is due to a viscosity effect. For comparison, the compound $C_6H_5SPF_4$, below −60 °C, is no longer undergoing rapid ligand reorganization and there is slow rotation about the P–S bond.[10]

Both **11** and **12** also undergo rapid intramolecular ligand exchange at room temperature. Their low-temperature ^{19}F NMR spectra, −90 to −100 °C, are broad absorptions, which may indicate that the reorganization process has been slowed.

Compound **13** was also prepared by allowing trichlorodiphenylphosphorane to react with trifluoroethoxide ion. It has a single broad absorption at ambient temperature in its ^{19}F NMR spectrum. At −30 °C two triplets, area 2:1, are found. Clearly the intramolecular reorganization process has been slowed on the NMR time scale. The $\Delta G^{\ddagger}$ for this process is 14 kcal/mol with a coalescence temperature of 20 °C. This finding is not unexpected, the corresponding triethoxy compound has also been shown to undergo slow ligand reorganization at reduced temperatures.[11]

One of the characteristic properties of pentaalkoxyphosphoranes is their ready exchange with 1,2-diols and catechols to give oxyphosphoranes containing one or two five-membered rings. It seemed of interest to test whether **11** would undergo a similar

11 + $HOCH_2CH_2OH$ ⟶ (O, O, $O-P(OCH_2CF_3)_3$) $\xrightarrow{HOCH_2CH_2OH}$

15

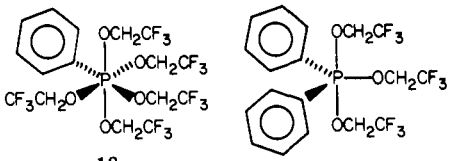
(O, O, $POCH_2CF_3$, O)$_2$

16

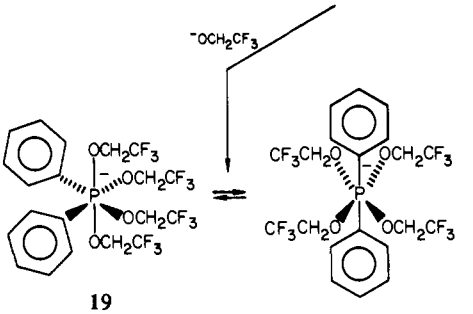
exchange. Treatment of **11** with 1 mol of ethylene glycol at room temperature led to essentially complete conversion into the monocyclic phosphorane **15**. Addition of another mole yielded **16**. These results indicate that a five-membered ring stabilizes an oxyphosphorane more effectively than two trifluoroethoxy groups.

With these phosphoranes in hand it seemed of interest to study the formation of hexacoordinated compounds from them. This has been done by allowing the phosphorane to react with sodium trifluoroethoxide ion in the presence of 18-crown-6 ether in benzene or by reaction with the salt in hexamethylphosphorictriamide. Treatment of **11** with 1 mol of trifluoroethoxide ion led to a solution which had two broad ^{31}P NMR resonances at δ −76.6 and −154.6. The first is due to unreacted **11**. The second resonance is assigned to the hexakis(trifluoroethoxy)phosphate ion **17**, the chemical shift of which is similar to that of the hexamethoxyphosphate ion (δ −144).[6] These findings show that **11** and **17** are in equilibrium with each other and that the rate of exchange is slow on the ^{31}P NMR time scale. When 2 mol of trifluoroethoxide ion were allowed to react with **11** under a variety of conditions, only **17** could be detected by ^{31}P NMR spectroscopy.

Treatment of **12** with 2 mol of trifluoroethoxide ion yielded a reaction mixture with one resonance at δ −156.2 in its ^{31}P NMR spectrum. This absorption is assigned to the monophenylphosphate **18**. This material should have two triplets in its ^{19}F NMR



18 **13**



19 **20**

spectrum in the ratio 4:1. In fact one large triplet is observed which is distorted by another smaller triplet.

When **13** was allowed to react with 2 mol of sodium trifluoroethoxide ion in benzene-d_6 in the presence of 18-crown-6 ether, two resonances at δ −155.7 and −159 were found in the ^{31}P NMR spectrum. The relative percentages were 82% and 18%, respectively. When the reaction was run in HMPA at 7 °C and the spectrum was recorded immediately after mixing the reagents, only one resonance was observed at δ −161.3. After the mixture was allowed to stand, another resonance began to appear at δ −157.7. This change was accompanied by the production of a large amount of the phosphoryl compound $(C_6H_5)_2P(O)OCH_2CF_3$ which absorbs at δ +34.7. These results coupled with those found in benzene show that the first product is the less stable and that isomerization occurs to the thermodynamically stable product. The ^{19}F NMR spectrum of a benzene solution containing mostly the isomer at δ −155 has one major triplet which is assigned to the trans isomer and two overlapping triplets that are assigned to the cis isomer. It is concluded that the cis isomer is the kinetic product and the trans is the thermodynamic product. Evidently the trifluoroethoxide ion attacks in the equatorial belt where the bond angles between the ligands are the largest. It approaches between a phenyl ring and a trifluoroethoxy group which is undoubtedly easier than attacking between the two phenyl groups. The trans isomer is probably thermodynamically favored over the cis for steric reasons. Very little is known about the stereochemistry of simple acyclic hexacoordinated phosphorus compounds. The compound $(CF_3)_2PF_4^-$ has been shown to have the trans configuration in solution.[12] Considerably more work is required before one can establish structural trends.

Treatment of **14** with 2 mol of trifluoroethoxide ion led to no change in the ^{31}P NMR spectrum after the solution had been allowed to stand at room temperature for 2 days. Whether the lack of reaction is due to a kinetic or thermodynamic effect has not been determined.

Compound **15**, when treated with sodium 2,2,2-trifluoroethoxide, yielded the hexacoordinated derivative **21** which was found to absorb at δ −128. Compound **16** yielded a mixture of two materials with chemical shifts at δ −102.2 and −105.9 in the ratio 1:2. The ^{13}C NMR spectrum has three doublets of approximately the same intensity which are assigned to the ring carbons of **22**

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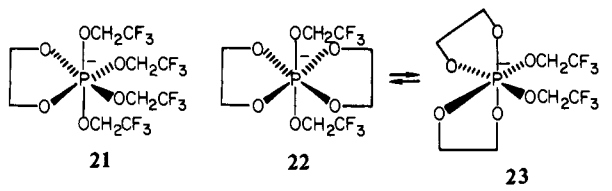
(12) (a) Bishop, E. O.; Carey, P. R.; Nixon, J. F.; Swain, J. R. *J. Chem. Soc. A* **1970**, 1074. (b) Jander, J.; Borner, D.; Englehardt, U. *Justus Liebigs Ann. Chem.* **1969**, *726*, 19.



21 22 23

and **23**. This spectrum shows that the cis isomer is the favored isomer, an observation which is in agreement with the findings of Tripett[8] and Ramirez.[7] It is interesting to note that whereas they found only the cis isomer, under thermodynamic conditions, substantial amounts of trans isomer are present in the equilibrium mixture of **22** and **23**. When the reaction was conducted at −23 °C and the ^{31}P NMR spectrum was recorded at this temperature, the ratio of trans to cis was found to be 1:1. After the reaction mixture was stirred overnight at room temperature, the ratio changed to 1:2. This result is very similar to those of Tripett.[8] It is interesting to note that previous studies of hexacoordinated phosphorus compounds where isomers were possible have always found only one isomer under equilibrium conditions. The present work shows that such is not always the case.

The upfield shift of the ^{31}P NMR resonance as one proceeds from **22** ⇄ **23**, to **21** to **17** is very similar to what is found in several oxyphosphorane series, and it may well be a helpful diagnostic tool.

Experimental Section

^1H NMR spectra were run on Varian Model A-60A, T-60, and FT-80 spectrometers. All chemical shifts are reported in ppm relative to tetramethylsilane. ^{13}C, ^{19}F, and ^{31}P NMR spectra were run on a Varian model FT-80 spectrometer equipped with a 10-mm, variable-temperature, broad-band probe. All ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane (internal). All spectra were obtained with use of full proton decoupling and a 35° flip angle. All ^{19}F chemical shifts are reported in ppm relative to fluorotrichloromethane (external), where a positive sign is downfield from the standard. All operations were carried out under an atmosphere of dry nitrogen. All solvents were scrupulously dried and freshly distilled.

Preparation of Tris(2,2,2-trifluoroethyl) Phosphite (6). Tris(2,2,2-trifluoroethyl) phosphite was prepared by the method of L. C. Krogh et al.[13] to yield 15.7 g (80%) of material; bp 144 °C (lit.[13] 130–131 °C).

Preparation of 2,2,2-Trifluoroethyl Benzenesulfenate (5). To a stirred solution of 5.5 g (55 mmol) and 5.55 g (55 mmol) of triethylamine in 75 mL of tetrahydrofuran was added at −20 °C 7.28 g (50 mmol) of benzenesulfenyl chloride.[14] The reaction mixture was allowed to warm to room temperature; it was stirred for 1 h and then filtered. After the solvent was removed under reduced pressure, the residual oil was distilled to yield 8.88 g (85%) of a yellow liquid; bp 47 °C (0.05 mm).

Preparation of Bis(2,2,2-trifluoroethyl) Phenylphosphonite (7). To a stirred solution of 34.8 g (0.19 mol) of dichlorophenylphosphine and 38.8 g (0.38 mol) of triethylamine in 200 mL of tetrahydrofuran was added, at −20 °C, 38.6 g (0.39 mol) of 2,2,2-trifluoroethanol. After being warmed to room temperature, the reaction mixture was filtered. After the solvent was removed under reduced pressure, the residual oil was distilled to yield 45.1 g (76%) of a colorless material; bp 48 °C (0.1 mm).

Preparation of 2,2,2-Trifluoroethyl Diphenylphosphinite (8). To a stirred solution of 85.3 g (0.39 mol) of chlorodiphenylphosphine and 38.6 g (0.39 mol) of triethylamine at −20 °C was added 38.6 g (0.39 mol) of 2,2,2-trifluoroethanol. The reaction mixture was allowed to warm to room temperature and then filtered. After the solvent was removed under reduced pressure, the residual oil was distilled to yield 83.4 g (76%) of a colorless oil; bp 130 °C (2.5 mm).

Preparation of Pentakis(2,2,2-trifluoroethoxy)phosphorane (11). To a stirred solution of 12.8 g (61.2 mmol) of 2,2,2-trifluoroethyl benzenesulfenate in 150 mL of pentane was added, at −78 °C, 10.0 g (30.6 mmol) of tris(2,2,2-trifluoroethyl) phosphite in 30 mL of pentane. The reaction mixture was allowed to warm to room temperature, and it was then stirred for 12 h. The solution was cooled to −20 °C and filtered. The filtrate was concentrated at reduced pressure, and the residual oil was distilled to yield 13.2 g (82%) of a colorless liquid; bp 44 °C (0.15 mm).

Preparation of Phenyltetrakis(2,2,2-trifluoroethoxy)phosphorane (12). To a stirred solution of 12.9 g (62 mmol) of 2,2,2-trifluoroethyl benzenesulfenate in 10 mL of pentane was added, at −78 °C, 9.49 g (31 mmol) of bis(2,2,2-trifluoroethyl) phenylphosphonite. The reaction mixture was allowed to warm to room temperature, and it was then stirred for 1 h. The mixture was cooled to −20 °C and filtered. The solvent was removed under reduced pressure and there remained 12.65 g (81%) of **12**. An analytical sample was obtained by sublimation (25 °C (0.05 mm)) to yield a white solid (mp 50 °C).

Preparation of Diphenyltris(2,2,2-trifluoroethoxy)phosphorane (13). To a solution of 8.06 g (66 mmol) of sodium 2,2,2-trifluoroethoxide in 50 mL of tetrahydrofuran at −40 °C was added 4.3 g (14.68 mmol) of diphenyltrichlorophosphorane[15] in 200 mL of dichloromethane. After being warmed to room temperature, the reaction mixture was stirred for 2 h. The solvent was removed under reduced pressure, and the residue was triturated with pentane. After filtration, the pentane was removed and the residue, 5.52 g (78%), crystallized. An analytical sample was prepared by sublimation (85 °C, (0.2 mm)); mp 63 °C.

The ^{19}F NMR spectrum ($CDCl_3$) at 30 °C showed one broad absorption centered at δ −80.7; at −20 °C there were two triplets at δ −80.2 (J_{FCCH} = 7.4 Hz) and δ −80.9 (J_{FCCH} = 7.4 Hz) in the ratio of 2:1.

Preparation of Triphenylbis(2,2,2-trifluoroethoxy)phosphorane (14). To a stirred solution of 12.2 g (58.4 mmol) 2,2,2-trifluoroethyl benzenesulfenate in 100 mL of pentane, at −78 °C, was added 7.66 g (29.2 mmol) of triphenylphosphine. After being warmed to room temperature, the reaction mixture was allowed to stir for 12 h. A solid (11.5 g, 86%) crystallized from the pentane, and it was separated by filtration. An analytical sample was obtained by sublimation (110 °C (0.2 mm)); mp 127–129 °C.

Preparation of Thiophenyltetrakis(2,2,2-trifluoroethoxy)phosphorane (10). To a stirred solution of 10 g (30.6 mmol) of tris(2,2,2-trifluoroethyl)phosphite in 100 mL of pentane was added, at −78 °C, 6.4 g (30.6 mmol) of 2,2,2-trifluoroethyl benzenesulfenate in 10 mL of pentane. After being warmed to room temperature, the reaction mixture was stirred for 1 h. After the solvent was removed there remained 12.1 g (74%) of a colorless oil **10**; bp 72 °C (0.15 mm).

Preparation of 2,2,2-Tris(2,2,2-trifluoroethoxy)-2,2-dihydro-1,3,2-dioxaphospholane (15). To a stirred solution of 4.83 g (9.18 mmol) of pentakis(2,2,2-trifluoroethoxy)phosphorane in 150 mL of dichloromethane at room temperature was added 0.57 g (9.18 mmol) of ethylene glycol in 50 mL of dichloromethane. After 12 h of stirring at room temperature, the solvent was removed under reduced pressure to yield 3.2 g (90%) of a white solid. An analytical sample was prepared by sublimation (35 °C (0.05 mm)); mp 42 °C.

Preparation of 16. To a stirred solution of 5.1 g (9.68 mmol) of pentakis(2,2,2-trifluoroethoxy)phosphorane in 150 mL of dichloromethane, at room temperature, was added 1.2 g (19.4 mmol) of ethylene glycol in 50 mL of dichloromethane. After 12 h of stirring, the solvent was removed to yield 2.1 g (86%) of a solid. An analytical sample was prepared by sublimation (55 °C (0.05 mm)); mp 59–60 °C.

Reaction of 11 with Sodium 2,2,2-Trifluoroethoxide. Method A. To a stirred solution of 1.7 g (3.32 mmol) of **11** in 2 mL of benzene-d_6 at 10 °C was added 0.45 g (3.32 mmol) of sodium 2,2,2-trifluoroethoxide and 0.88 g (3.32 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6. After 30 min of stirring at 10 °C, the ^{31}P NMR spectrum had two resonances of equal size at δ −76.6 and δ −154.6. To this was then added 0.45 g (3.32 mmol) of sodium 2,2,2-trifluoroethoxide and 0.88 g (3.32 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6 with the results: ^{31}P NMR (C_6D_6) δ −154.6; ^{19}F NMR (C_6D_6) δ −81.2 (t, J_{FCCH} = 9.7 Hz); ^1H NMR (C_6D_6) δ 4.42 (dq, J_{HCOP} = 6 Hz, J_{HCCF} = 9.7 Hz); ^{13}C NMR (C_6D_6) δ 63.7 (dq, J_{COP} = 9.2 Hz, J_{CCF} = 32.6 Hz), δ 127.1 (dq, J_{CCOP} = 14.7 Hz, J_{CF} = 278.1 Hz).

Method B. To a stirred solution of 1.43 g (2.7 mmol) of **11** in 1 mL of hexamethylphosphorictriamide at 20 °C was added 0.64 g (5.4 mmol) of sodium 2,2,2-trifluoroethoxide in 2 mL of the same solvent: ^{31}P(external lock) δ −154.4; ^{19}F(external lock) δ −75.9 (t, J_{FCCH} = 9.6 Hz).

Reaction of 12 and Sodium 2,2,2-Trifluoroethoxide. Method A. To a stirred solution of 0.53 g (1.05 mmol) of **12** in 2 mL of benzene-d_6, at 10 °C, was added 0.26 g (2.1 mmol) of sodium 2,2,2-trifluoroethoxide and 0.55 g (2.1 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6. After 1 h of stirring at 10 °C, the following spectral data were obtained: ^{31}P NMR (C_6D_6) δ −156.2; ^{19}F NMR (C_6D_6) δ −80.25 (t, J_{FCCH} = 9.8 Hz).

Method B. To a stirred solution of 0.53 g (1.05 mmol) of **12** in 2 mL of hexamethylphosphorictriamide was added 0.26 g (2.1 mmol) of sodium 2,2,2-trifluoroethoxide in 8 mL of the same solvent. After 1 h of stirring at room temperature, the following ^{31}P spectral data were obtained: ^{31}P(external lock) −156.3.

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Reaction of 13 with Sodium 2,2,2-Trifluoroethoxide. Method A. To a stirred solution of 0.52 g (1.08 mmol) of **13** in 2 mL of benzene-d_6 was added, at 10 °C, 0.26 g (2.15 mmol) of sodium 2,2,2-trifluorethoxide and 0.57 g (2.15 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6. The following spectral data were obtained after 5 min of stirring: ^{31}P (C_6D_6) δ −155.7 (82%), −159 (18%). The ^{19}F NMR spectrum has a major resonance at δ −80.01 (J_{FCCH} = 10 Hz) and two triplets at δ −74.85 (J_{FCCH} = 8.5 Hz) and −75.00 (J_{FCCH} = 10.6 Hz).

Method B. To a stirred solution of 0.52 g (1.08 mmol) of **13** in 2 mL of hexamethylphosphorictriamide, at 10 °C, was added 0.33 g (2.7 mmol) of sodium 2,2,2-trifluoroethoxide in 2 mL of the same solvent. Immediately after mixing the ^{31}P NMR spectral data were obtained: ^{31}P NMR (external lock, 7 °C) δ −161.3.

Reaction of 14 with Sodium 2,2,2-Trifluoroethoxide. To a stirred solution of 0.24 g (0.52 mmol) of **14** in 2 mL of benzene-d_6 was added, at 10 °C, 0.13 g (1.04 mmol) of sodium 2,2,2-trifluoroethoxide and 0.28 g (1.04 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6. The progress of the reaction was monitored by observing the ^{31}P NMR spectrum in C_6D_6: 2 days at room temperature, δ −58.5; 1 day at 36 °C, δ 24.7 (triphenylphosphine oxide, 10%), δ −58.5 (90%); 2 days at 36 °C, δ 24.7.

Reaction of 15 with Sodium 2,2,2-Trifluoroethoxide. To a stirred solution of 0.43 g (1.1 mmol) of **15** in 2 mL of benzene-d_6 was added, 10 °C, 0.27 g (2.2 mmol) of sodium 2,2,2-trifluoroethoxide and 0.58 g (2.2 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6. After 10 min of stirring, the only absorption in the ^{31}P NMR spectrum was at δ −128.0.

Reaction of 16 with Sodium 2,2,2-Trifluoroethoxide. To a stirred solution of 0.4 g (1.6 mmol) of **16** in 2 mL of benzene-d_6 was added, at room temperature, 0.39 g (3.2 mmol) of sodium 2,2,2-trifluoroethoxide and 0.85 g (3.2 mmol) of 18-crown-6 ether in 2 mL of benzene-d_6. After 30 min of stirring at room temperature the ^{31}P NMR spectrum (C_6D_6) showed two absorptions at δ −102.2 (33%) and −105.9 (67%). The ^{13}C NMR spectrum shows strong absorptions for the 18-crown-6 ether and excess salt as well as complicated multiplets due to coupling to fluorine; however there are three equal-sized doublets which are well resolved. A possible assignment is δ 59.2 (d, J_{COP} = 15.7 Hz) and δ 59.5 (d, J_{COP} = 22 Hz) for the methylene carbons of the cis isomer and δ 59.6 (d, J_{COP} = 11.6 Hz) for the methylene carbons of the trans isomer. In a similar experiment, using toluene-d_8 as the solvent, conducted at −23 °C the following spectral data were obtained: ^{31}P NMR (toluene-d_8) δ −102.2 (50%) and δ −105.9 (50%). After the reaction mixture was warmed to room temperature overnight, the relative precentages became 33:66.

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Formation of the Crossed Product 1,4-Disubstituted 2,3,5,6,11-Pentaoxabicyclo[5.3.1]undecane from a Mixture of Two Kinds of Ozonides in the Presence of an Acid Catalyst. Elucidation of the Intermediates in the Acidolysis of an Ozonide

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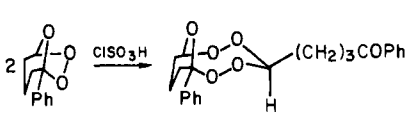
Abstract: The reaction of a mixture of two kinds of ozonides in the presence of an acid catalyst gives the crossed 2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane derivative. When a mixture of 3-phenylindene ozonide (**1a**) and stilbene ozonide (**1e**), for example, was treated with 0.03 mol equiv of $ClSO_3H$ or $SbCl_5$, 1,4-diphenyl-9,10-benzo-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**18**) was obtained. Consistent with this result, the reaction of **1e** with a zwitterionic intermediate **3a** (prepared by treating **1a** with 1 mol equiv of $SbCl_5$) gave **18** in a yield of 10%. These results have been explained by considering a mechanism which involves the initial attack of **3a** (when the catalyst is $SbCl_5$) or a similar intermediate **2a** with a carboxonium ion structure (in the case of $ClSO_3H$) on another ozonide. However, the reaction of a mixture of 1-phenylcyclopentene ozonide (**1b**) and 1-methylcyclopentene ozonide (**1c**) gave 1-methyl-4-*exo*-(3-benzoylpropyl)-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**20**) as the sole crossed product. Consistent with this, the reaction of **1c** with a zwitterionic intermediate **3b** (prepared by treating **1b** with 1 mol equiv of $SbCl_5$) gave the same product **20**. The participation of the $SbCl_5$-complexed carbonyl oxide **5b** (when the catalyst is $SbCl_5$) or the protonated carbonyl oxide **4b** (in the case of $ClSO_3H$) has been postulated to explain the result. As the model species for these postulated intermediates, the carboxonium ion **2m** and the protonated carbonyl oxide **4m** have been investigated with an ab initio SCF–MO method.

Because of its unique structure, the chemistry of an ozonide (1,2,4-trioxolane) is expected to be promising. However, the synthetic use has been limited hitherto to the syntheses of ring-contraction products by thermolysis or photolysis.[2] Recently we have reported that the reaction of 1-phenylcyclopentene ozonide (**1b**) with catalytic amounts of $ClSO_3H$ gave 1-phenyl-4-*exo*-(3-benzoylpropyl)-2,3,5,6,11-pentaoxabicyclo[5.3.1]undecane (**6b**) (eq 1);[3,4] this result seems to be novel because not only does the



1b **6b** (1)

peroxide **6b** fall into a new category of cyclic peroxides[5] but also the formation of an eight-membered ring by cyclization is well-known to be quite difficult.[6] To explain the formation of **6b**, we

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