at 5.89 × 10^{-3} M and varying the concentration of the phenol from 1.68 × 10^{-4} M (IA_1) to 1.68 × 10^{-6} M (IA_2), we obtain the following ratios of equilibrium constants: $K_{eq_{PNP}}(IA_1)/K_{eq_{PNP}}(IA_2) = 1.08$, $K_{eq_{PNP}}'(IA_1)/K_{eq_{PNP}}'(IA_2) = 1/46.6$, $K_{eq_{PNP}}^{A}(IA_1)/K_{eq_{PNP}}^{A}(IA_2) = 1.01$, $K_{eq_{PNP}}^{A'}(IA_1)/K_{eq_{PNP}}^{A'}(IA_2) = 1/49.9$. If method IB is employed, with the phenol concentration held constant at 8.42 × 10^{-5} M and the base concentration is varied from 1.18 × 10^{-2} M (IB_1) to 1.18 × 10^{-4} M (IB_2), we obtain the ratios: $K_{eq_{PNP}}(IB_1)/K_{eq_{PNP}}(IB_2) = 1/2.5$, $K_{eq_{PNP}}'(IB_1)/K_{eq_{PNP}}'(IB_2) = 1/10.9$, $K_{eq_{PNP}}^{A}(IB_1)/K_{eq_{PNP}}^{A}(IB_2) = 22.5$, $K_{eq_{PNP}}^{A'}(IB_1)/K_{eq_{PNP}}^{A'}(IB_2) = 7.22$. Use of the second method (II) where the concentration of the base at 1.18 × 10^{-2} M and the phenol at 1.68 × 10^{-4} M (II_1) is diluted 10-fold to a base concentration of 1.18 × 10^{-3} M and phenol concentration of 1.68 × 10^{-5} M (II_2) followed by a subsequent dilution of 10-fold to concentrations of 1.18 × 10^{-4} M for the base and 1.68 × 10^{-6} M for the phenol (II_3) gave rise to the following ratios: $K_{eq_{PNP}}(II_1)/K_{eq_{PNP}}(II_2) = 1/1.19$, $K_{eq_{PNP}}'(II_1)/K_{eq_{PNP}}'(II_2) = 1/11.1$, $K_{eq_{PNP}}^{A}(II_1)/K_{eq_{PNP}}^{A}(II_2) = 8.6$, $K_{eq_{PNP}}^{A'}(II_1)/K_{eq_{PNP}}^{A'}(II_2) = 1.11$; and $K_{eq_{PNP}}(II_2)/K_{eq_{PNP}}(II_3) = 1.08$, $K_{eq_{PNP}}'(II_2)/K_{eq_{PNP}}'(II_3) = 1/9.6$, $K_{eq_{PNP}}^{A}(II_2)/K_{eq_{PNP}}^{A}(II_3) = 10.6$, $K_{eq_{PNP}}^{A'}(II_2)/K_{eq_{PNP}}^{A'}(II_3) = 1.05$. It appears, then that the selection of the dissociation scheme represented by eq 7 as the one which is more nearly correct can be successfully sustained.

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(34) A. C. Satterthwait and W. P. Jencks, *J. Am. Chem. Soc.*, **96**, 7018 (1974), and references quoted therein.

(35) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms", Vol. I, W. A. Benjamin, New York, N.Y., 1966, p 46.

(36) W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, N.Y., 1969, pp 67, 484.

(37) P. Y. Bruice and T. C. Bruice, *J. Am. Chem. Soc.*, **96**, 5533 (1974).

(38) H. A. Sober, Ed., "Handbook of Biochemistry Selected Data for Molecular Biology", The Chemical Rubber Co., Cleveland, Ohio, 1968, p J158.

(39) K. Ekelin and L. G. Sillén, *Acta Chem. Scand.*, 7, 987 (1953).

(40) The LPDE system strongly catalyzes the aminolysis of *p*-nitrophenyl acetate by virtue of the much stronger interaction of its ion pairs and higher ionic aggregates with the highly polar transition state than with the weakly polar initial state. The repeated finding that $\Delta\Delta H^{\ddagger} \simeq 0$ for these powerful salt effects is both fascinating and important. We wish to postpone a more detailed analysis of the data until our physico-chemical characterization of these unusual electrolytic solutions is more complete. One line of reasoning would be that the negative enthalpy term for electrostatic stabilization is apparently offset by a positive enthalpy term for the release of ether molecules but no such complete compensatory effect occurs in the respective entropy of activation terms. In some sense, the increase in $\Delta\Delta S^{\ddagger}$ represents a partial utilization of electrostatic energy in such a way as to facilitate the attainment of the transition state. The group of observations as a whole reveals a number of features which could provide mechanisms for rate acceleration and specificity.[41]

(41) W. P. Jencks, *Adv. Enzymol. Relat. Areas Mol. Biol.*, **43**, 219 (1975).

Some Acyclic Pentaalkoxyphosphoranes

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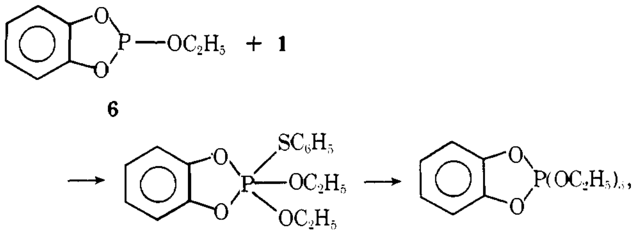
Abstract: Methyl, ethyl, isopropyl, neopentyl, cyclopentyl, cyclohexyl, and benzyl benzenesulfenates have been allowed to react respectively with trimethyl, triethyl, triisopropyl, trineopentyl, tricyclopentyl, tricyclohexyl, and tribenzyl phosphites. In all cases pentaalkoxylphosphoranes were formed. Varying degrees of stability have been found for these substances. They have been characterized by ^1H, ^{31}P, and ^{13}C NMR. Several of them have been investigated by variable-temperature ^1H and ^{13}C NMR. In no case was it possible to detect a nonequivalency of any particular group of atoms.

Methods for the preparation of acyclic pentaalkoxyphosphoranes have been few in number. It has been shown that dialkyl peroxides such as dimethyl and diethyl peroxide will react with trialkyl phosphites to give pentaalkoxyphosphoranes.[1-12] This reaction is limited by the availability of the peroxides and their inherent danger. Pentaphenoxyphosphorane has been prepared by allowing phenol to react with phosphorus pentachloride in the presence of organic bases.[13] Attempts to form pentaethoxyphosphorane from tetraethoxyphosphonium tetrafluoroborate and ethoxide ion have never led to the production of an observable amount of phosphorane.[14] The dialkyl peroxide-trialkyl phosphite reaction is thought to proceed by a biphilic insertion of the phosphorus into the oxygen-oxygen bond.[8] This route by-passes a tetraethoxyphosphonium ethoxide ion pair which would most probably decompose into diethyl ether and triethyl phosphate.

Because of the instability of acyclic pentaalkoxyphosphoranes, it seems that only high-energy reactants can offer much potential for their synthesis. Secondly, only paths which do not offer the opportunity for phosphate formation can be used. In a search for reactants that can provide the potential for phosphorane formation, a number of substances with weak σ bonds have been investigated. One of these materials was ethyl benzenesulfenate (**1**). When **1** was allowed to react with triethyl phosphite (**2**), a rapid reaction occurred with the production of pentaethoxyphosphorane (**3**) and diphenyl disulfide (**4**):[15]

$$\begin{array}{ccccccc} 2C_6H_5SOC_2H_5 & + & (C_2H_5O)_3P & \rightarrow & (C_2H_5O)_5P & + & (C_6H_5S)_2 \\ \mathbf{1} & & \mathbf{2} & & \mathbf{3} & & \mathbf{4} \end{array}$$

This rather remarkable reaction presumably involves the initial production of a mixed phosphorane, $(C_2H_5O)_4PSC_6H_5$ (**5**), which rapidly reacts with another mole of **1** to yield **3** and **4**. In fact, **5** has never been observed. A mixed thiooxyphosphorane **7** was observed when ethyl 1,2-phenylene phosphite (**6**) was allowed to react with **1**. An absorption was found at δ +22 relative to 85% phosphoric acid in the ^{31}P NMR spectrum. This material is assigned the structure **7** primarily on the basis of its ^{31}P NMR spectrum. It is known that substitution of sulfur for oxygen in an oxyphosphorane leads to a downfield shift of the ^{31}P NMR resonance. The pentaalkoxyphosphorane **8** which resulted from the further reaction of **7** with **1** absorbs at δ +50.



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7

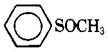
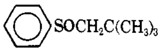
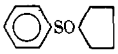
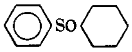
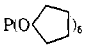
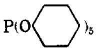
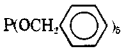
8

These rather remarkable results prompted an investigation of the general utility of the reaction as a means of preparing phosphoranes.

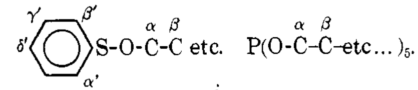
Results and Discussion

A series of alkyl benzenesulfenates, **1**, **9–14**, was prepared by condensation of benzenesulfenyl chloride with the appro-

Table I. NMR Spectral Data[a]

	^{1}H NMR					^{13}C NMR								^{31}P
Compound	α	β	γ	δ	Aromatic	α	β	γ	δ	α′	β′ or γ′		δ′	NMR
SOCH$_3$	3.55				7.21	65.2				140.1	124.2	128.9	126.7	
SOCH$_2$CH$_3$	3.72 (7)	1.12 (7)			7.17	73.9	15.9			141.0	123.6	128.9	126.3	
SOCH(CH$_3$)$_2$	3.83 (6)	1.26 (6)			7.25	80.1	22.6			141.9	123.0	128.8	126.0	
SOCH$_2$C(CH$_3$)$_3$	3.46			0.90	7.23	88.9	32.9	26.3		140.8	123.6	128.8	126.3	
SO	4.10		1.65		7.00	89.5	33.4	23.6		141.6	123.2	128.8	125.9	
SO	3.37			1.57	7.20	85.2	32.8	23.9	25.6	142.3	122.6	128.8	125.7	
SOCH$_2$	4.62				7.10									
P(OCH$_3$)$_5$	3.46 (12)					54.7 (11.7)								+66
P(OCH$_2$CH$_3$)$_5$	3.80 (7,7)	1.13 (7,2)				61.5 (11.5)	15.8 (8.5)							+69
P[OCH(CH$_3$)$_2$]$_5$	4.35 (6,8)	1.25 (6,1)				68.5 (12.8)	24.1 (6.3)							+69
P[OCH$_2$-C(CH$_3$)$_3$]$_5$	3.63 (4.4)			0.93		77.1 (13.4)	33.4 (9.6)	27.0						+72
P(O)$_5$	4.57		1.60			78.3 (12.8)	34.8 (6.1)	24.1						+75
P(O)$_5$	4.09			1.60		74.3 (13.2)	34.6 (5.3)	24.8	26.4					+74
P(OCH$_2$)$_5$	4.87 (8)				7.10									+68

[a] The numbering system is as shown in i. In the ^{1}H NMR spectra all integrated areas are correct, to better than 10%. The aromatic hydrogens, in all cases, show complex multiple absorptions. The ^{13}C NMR spectra are fully proton decoupled. The coupling constants listed in parentheses are J_{HCCH}, J_{HCOP}, J_{HCCOP}, J_{COP}, and J_{CCOP}.



i

priate alcohol in the presence of triethylamine. The alkyl benzenesulfenates are relatively stable materials, and they can be stored after distillation.

$$2C_6H_5SOR + (RO)_3P \rightarrow (RO)_5P + (C_6H_5S)_2$$
$$\mathbf{9}, R = CH_3;\ \mathbf{10}, R = CH(CH_3)_2$$
$$\mathbf{11}, R = CH_2C(CH_3)_3;\ \mathbf{12}, R = c\text{-}C_5H_9$$
$$\mathbf{13}, R = c\text{-}C_6H_{11};\ \mathbf{14}, R = CH_2C_6H_5$$

They do rearrange readily to the appropriate sulfoxide in the presence of acid. The yields of these materials have not been optimized. On a small scale they are usually at least 50%. In the case of methyl benzenesulfenate, a 90% yield has been obtained on a 125-g scale. The alkyl benzenesulfenates have been characterized by their ^{1}H and ^{31}C NMR spectra (Table I), their mass spectra, and their characteristic absorption in the infrared at around 1580 cm^{-1} which is absent in the isomeric sulfoxides. The isomeric sulfoxides also have a strong absorption at ca. 1050 cm^{-1}. The isomeric sulfenates may show an absorption in this region. No absorptions have been observed in this region which are as strong as those of sulfoxides. Further characterization rests upon the fact that the sulfenates react to give phosphoranes while sulfoxides do not. Benzyl benzenesulfenate could not be distilled. It decomposed on attempted distillation, and thus it was necessary to work with the crude material. In preliminary experiments, compounds **9–13** were alllowed to react with either methyl or ethyl 1,2-phenylene phosphite. The purpose of these experiments was to determine whether phosphoranes were formed or not. Phosphoranes derived from alkyl 1,2-phenylene phosphites tend to be much more stable than simple acyclic ones, and thus if they were not formed it did not seem likely that phosphoranes would be formed from simple trialkyl phosphites. In each case the ^{31}P NMR spectrum indicated that a phosphorane had been formed in high yield.

The phosphites, **2, 15–20** (**15**, R = CH$_3$; **2**, R = CH$_3$CH$_2$; **16**, R = CH(CH$_3$)$_2$; **17**, R = CH$_2$C(CH$_3$)$_3$; **18**, R = c-C$_5$H$_9$; **19**, R = c-C$_6$H$_{11}$; **20**, R = CH$_2$C$_6$H$_5$), were either prepared or obtained from commercial sources. The alkyl benzenesulfenate and trialkyl phosphite were allowed to react in pentane at −78 °C. In each case a phosphorane was formed. Pentamethoxyphosphorane (**21**) had been prepared before;[2] however, only its ^{1}H NMR spectrum had been recorded. In the present work **21** has been found to have an absorption at δ +66 in its ^{31}P NMR spectrum. ^{1}H and ^{13}C NMR data can be found in Table I. Pentaethoxyphosphorane (**3**) was prepared on a number of occasions by this route, and its spectral properties are recorded in Table I. Compound **3** can be distilled under reduced pressure. Unfortunately, distillation did not free it from triethyl phosphate which was formed as a contaminant. In fact, purification of these oxyphosphoranes is the most difficult aspect of working with them. A modification of the technique introduced by Jones[5] is usually the most successful. After the reaction of the phosphite and alkyl benzenesulfenate is complete as evidenced by ^{31}P NMR measurements, the pentane solution is usually concentrated to ca. 0.5 M in oxyphosphorane, and the solution is then extracted with several volumes of propylene carbonate. The propylene carbonate removes phosphates and any secondary phosphite that might be present as well as most of the diphenyl disulfide. In the early phases of this work, diphenyl disulfide was removed by low-temperature filtration of the pentane solution.

It was never possible to remove all of the diphenyl disulfide by filtration, and the manipulations invariably led to the production of phosphates by hydrolysis. Because of the difficulties associated with manipulating these materials and because of their hydrolytic and thermal instability, their structure assignments rest in the main on their ^{1}H, ^{13}C, and ^{31}P NMR spectra. All of these data are in agreement with the assigned structures. Where possible, comparison of these data with data obtained from phosphoranes prepared by the peroxide route have shown the data to be identical.[2,5] Low-temperature filtration of a solution of pentaethoxyphosphorane (**21**) led to an oil of greater than 80% purity. Pentaneopentyloxyphosphorane, (**23**), pentacyclopentyloxyphosphorane (**24**), and pentacyclohexyloxyphosphorane (**25**) were isolated as white crystalline solids. Compounds **23** and **24** were stored in a refrigerator for over 3 months with essentially no decomposition. Compound **25** was not nearly so stable. It was stable for 1 month in a refrigerator. After 2 months, 50% of the material had decomposed. Pentamethoxyphosphorane is quite stable, and it can be heated at 80 °C for 3 days with very little decomposition. If the oxyphosphoranes are not purified, rapid decomposition to phosphates occurs within a few days. Pentaisopropyloxyphosphorane (**22**) showed varying degrees of stability. There is no doubt that it is less stable than **23, 24,** and **25.** It is difficult to assess the inherent stability of these materials because traces of impurities can cause their decomposition. Pentabenzyloxyphosphorane (**26**) was prepared in carbon tetrachloride solution. After 0.5 h at room temperature, the reaction was complete, and there was present ca. 50% of tribenzyl phosphate as evidenced by an absorption at δ 0 ppm in the ^{31}P NMR spectrum of the reaction mixture. There was also present 50% of pentabenzyloxyphosphorane (**26**). This material has an absorption at δ +69 ppm in its ^{31}P NMR spectrum. After 5 days at room temperature, complete decomposition to the phosphate had occurred. Of course all of the pentaalkoxyphosphoranes are hydrolytically unstable.

The results of this preparative investigation clearly demonstrate that the alkyl benzenesulfenate route is currently the best method for the preparation of simple acyclic pentaalkoxyphosphoranes. No complete study has been conducted on optimizing the yields of these materials. Pentamethoxyphosphorane has been prepared in ca. 60% yield on a 10-g scale. Studies in progress in this laboratory indicate that the reaction can be utilized to prepare a variety of cyclicoxyphosphoranes, and thus the reaction shows considerable promise as a general route to pentaoxyphosphoranes.

One of the most interesting aspects of phosphorane chemistry is the intramolecular permutational isomerization which many of them undergo.[17] It is believed that simple nonring containing phosphoranes prefer to exist as trigonal bipyramids (TBP) and that they isomerize via tetragonal pyramidal (TP) transition states. This assumption is not generally applicable, and phosphoranes in which the phosphorus is incorporated in rings may prefer to exist as tetragonal pyramids or structures in between TBP and TP.[18,19]

The ^{13}C NMR spectra of **3, 21, 22, 23,** and **24** show only one kind of carbon for each type at room temperature. Extensive variable-temperature ^{13}C NMR measurements on **22, 23, 24,** and **25** down to as low as −100 °C have not led to any significant changes in the spectra. In the case of **22**, low-temperature ^{1}H NMR measurements did not lead to any observable alteration in the spectrum. Unfortunately, these negative results really do not permit any positive interpretation. One does not know how large the chemical shift difference between an apical P–O–C carbon and an equatorial P–O–C carbon might be, and so it is not possible to conclude anything about the rates of intramolecular permutational isomerization of these compounds. It is interesting to note in this regard that $(C_6H_5)_2P(OCH_2CH_3)_3$ (**27**) shows a change in its ^{1}H NMR spectrum on lowering the temperature. The change has been attributed to inhibition of permutational isomerization.[4] This compound has been reinvestigated by variable-temperature ^{13}C NMR, and coalescence of the resonances of the carbons of the methylene groups was found at −19 °C with a maximum chemical shift difference of 127 Hz at −80 °C.[20] Of course, **27** is not a pentaalkoxyphosphorane and the phenyl groups prefer to adopt equatorial dispositions. The phenyl groups also undoubtedly affect the chemical shift differences between the apical P–O–C carbon and the equatorial P–O–C carbon. This was certainly true in the case of the hydrogens bonded to these carbons. Quite recently, Westheimer and co-workers[21] have studied the pseudorotation of the sterically hindered phosphorane, methyltetrakis(2,6-dimethylphenoxy)phosphorane. They found the activation energy for the ligand reorganization to be 7.7 kcal/mol, whereas that of **27** is 12 kcal/mol. Dimethyltris(*o*-cresoxy)phosphorane has an activation energy for its ligand reorganization of only 5.8 kcal/mol. These values certainly suggest that pentaalkoxyphosphoranes will have even lower activation energies for ligand reorganization, and it is perhaps not surprising that it has not been possible to determine them.

One of the most valuable means of characterizing pentaalkoxyphosphoranes has been by ^{31}P NMR spectroscopy. These materials usually absorb upfield from their tricoordinate and tetracoordinate relatives. Their ^{1}H and ^{13}C NMR spectra are also characteristic and can be used for identification purposes. In the series phosphite, phosphate, pentaalkoxyphosphorane, hydrogens on the α carbon (i.e., POCH of the phosphite) generally absorb upfield of those of the pentaalkoxyphosphorane which in turn absorb up field of the phosphate. Usually the P–OCH coupling of the phosphorane and phosphite are larger than that of the phosphate. In the case of ^{13}C NMR spectra, the POC coupling for the phosphites and pentaalkoxyphosphoranes is about twice that of the phosphate. The POC coupling of the phosphoranes is slightly larger than that of the phosphite.

The reactions of a variety of other trivalent phosphorus compounds with ethyl benzenesulfenate have been investigated. Phenyldimethylphosphine, diphenylmethylphosphine, and tri-*n*-butylphosphine all react to give the corresponding phosphine oxides. Diethyl peroxide reacts with these materials to give phosphoranes which are in equilibrium with the phosphonium ethoxides. Triphenylphosphine, ethyl diphenylphosphinite, and diethyl phenylphosphonite react with ethyl benzenesulfenate in pentane to give solutions of the pentacoordinate phosphorus compounds contaminated with varying amounts, usually less than 25%, of the corresponding phosphoryl compound. These compounds had been prepared before from the same phosphorus containing reactants and diethyl peroxide. Both methods give mixtures of the pentacoordinate compound and the appropriate phosphoryl compound. Of course the alkyl benzenesulfenate route also produces a mole of diphenyl disulfide which is not necessarily easily removed.

The mechanism of the formation of the phosphoranes is certainly not obvious, and experiments are now under way to try to learn more about it. Similarly the broad applicability of the method for the production of phosphoranes is being studied.

Experimental Section

^{1}H NMR spectra were obtained with Varian T-60, HA-100, HR-220, and JEOL MH-100 instruments. Chemical shift values are reported in ppm relative to internal tetramethylsilane. ^{31}P NMR spectra were obtained with Varian HA-100 and Varian CFT-20 instruments. Chemical shifts are reported in ppm relative to the external standard, 85% phosphoric acid. ^{13}C NMR spectra were obtained with a Varian CFT-20 NMR spectrometer. Chemical shifts are reported relative to internal tetramethylsilane in ppm.

Materials. Trimethyl phosphite, triethyl phosphite, and triisopropyl phosphite were obtained from commercial sources; they were distilled from sodium prior to use. Benzenesulfenyl chloride was prepared in 95.4% yield by the procedure of Lecher et al.[22]

Tricyclopentyl Phosphite (18). Tricyclopentyl phosphite has been prepared by Davies et al. from cyclopentanol and tris(dimethylamino)phosphine.[23] The procedure used in this work involved heating a mixture of 1650 mL of ether, 41.2 g (0.30 mol) of phosphorus trichloride, 110 g (0.90 mol) of *N,N*-dimethylaniline, and 77.4 g (0.90 mol) of cyclopentanol under reflux for 48 h. The precipitated *N,N*-dimethylaniline hydrochloride was separated by forcing the reaction solution through a filter stick. The ether was evaporated, and the residue was distilled from metallic sodium, bp 105 °C (0.25 mm) [lit.[23] 102–104 °C (0.1 mm)]. The spectral properties are reported in Table I.

Tricyclohexyl Phosphite (19). Tricyclohexyl phosphite has been prepared by Arbusov and Valitova[24] as a hygroscopic solid of broad melting point range. Saunders and Stark obtained **19** as a liquid.[25] The same procedure and molar quantities as used in the preparation of **18** yielded a semisolid which was recrystallized from acetonitrile. The solid was dried over sulfuric acid. The material has mp 53–54 °C: This material is extremely hygroscopic, and it should be stored at 0 °C under argon.

Trineopentyl Phosphite. This material was prepared according to the procedure of Relles.[26]

Preparation of Methyl Benzenesulfenate (9). Methyl benzenesulfenate has been prepared by Vorlander and Mittag[27] in rather poor yield. The following procedure yields **9** in excellent yield. There was added to a 2-L three-necked flask, equipped with a mechanical stirrer and a dropping funnel,11500 mL of anhydrous ether, 111 g (1.1 mol) of triethylamine, which had been treated with potassium hydroxide pellets, and 35 g (1.1 mol) of spectrograde methanol, which had been dried over 3A Linde molecular sieve. The mixture was cooled in an ice–salt bath under an atmosphere of nitrogen. To the chilled mixture was added dropwise over 2 h with vigorous stirring 144.5 g (1.0 mol) of benzenesulfenyl chloride. At the end of the addition, the mixture was filtered to remove the precipitated triethylamine hydrochloride. The filter cake was washed with two 150-mL portions of ether; the ether was evaporated in vacuo, and the residue was distilled, bp 47 °C (0.25 mm) [lit.[27] bp 88–89 °C (4.0 mm)], to yield 126.4 g (90%) of **9**.

Ethyl Benzenesulfenate (1). Compound **1**, bp 45–46 °C (0.53 mm) was obtained in 75% yield. The mass spectrum had a molecular ion *m/e* 154.

Anal. Calcd for $C_8H_{10}OS$: C, 62.29; H, 6.53. Found: C, 62.03; H, 6.53.

Isopropyl Benzenesulfenate (10). Compound **10**, bp 54–58 (0.6 mm), was obtained in 48% yield. The mass spectrum had a molecular ion *m/e* 168.

Anal. Calcd for $C_9H_{12}OS$: C, 64.28; H, 7.14. Found: C, 64.20; H, 7.13.

Neopentyl Benzenesulfenate (11). Compound **11**, bp 58 °C (0.05 mm), was prepared in 68% yield. The mass spectrum had a molecular ion *m/e* 196.

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.29; H, 8.21. Found: C, 67.35; H, 8.16.

Cyclopentyl Benzenesulfenate (12). Compound **12**, bp 78 °C (0.10 mm), was obtained in 57% yield. The mass spectrum had a molecular ion *m/e* 194.

Anal. Calcd for $C_{11}H_{14}SO$: C, 67.99; H, 7.26. Found: C, 68.08; H, 7.27.

Cyclohexyl Benzenesulfenate (13). Compound **13**, bp 88 °C (0.15 mm), was obtained in 54% yield. The mass spectrum had a molecular ion *m/e* 208.

Anal. Calcd for $C_{12}H_{16}OS$: C, 69.18; H, 7.74. Found: C, 69.35; H, 7.67.

Preparation of Pentamethoxyphosphorane (21). Methyl benzenesulfenate (2.33 g, 0.0166 mol) in 5 mL of dry pentane was added over a period of 30 min to a solution of 1.03 g (0.0083 mol) of trimethyl phosphite in 5 mL of pentane at −78 °C. Shortly after the addition, the solution was separated from the precipitated diphenyl disulfide at −78 °C using a filter stick. The pentane was removed in a stream of nitrogen at room temperature to give an oil. The ^{31}P NMR spectrum indicated 85% pentamethoxyphosphorane with an absorption at +66 and 15% trimethyl phosphate with an absorption at +2. Other spectral data can be found in Table I.

More recently, larger quantities of **21** have been prepared by the following procedure. To 23.03 g (0.1645 mol) of methyl benzenesulfenate in 250 mL of anhydrous pentane at −78 °C was added with stirring over 1 h a solution of 10.21 g (0.0823 mol) of trimethyl phosphite in 50 mL of anhydrous pentane. The reaction mixture which contained precipitated diphenyl disulfide was allowed to warm to room temperature and stirred for 1 h. The solution was cooled in an acetone–dry ice bath, and the diphenyl disulfide which crystallized was separated by forcing the solution through a filter stick. The diphenyl disulfide was washed twice with 50-mL portions of propylene carbonate. The pentane solutions were combined, and the pentane was removed in vacuo. The residue, a light-yellow oil, weighed 8.69 g (ca. 57%). The ^{1}H and ^{31}P NMR spectra showed it to be essentially pure pentamethoxyphosphorane. It did contain small amounts of pentane and diphenyl disulfide. The mass spectrum of this material showed as the highest molecular weight mass fragment that of trimethyl phosphate.

Preparation of Pentaethoxyphosphorane (3). Triethyl phosphite (1.50 g, 0.0091 mol) was added at −78 °C with stirring to a solution of 3.40 g (0.0022 mol) of ethyl benzenesulfenate in 10 mL of pentane. The reaction mixture was allowed to warm to room temperature with stirring. After being at room temperature for 2 h it was cooled to −20 °C, and the diphenyl disulfide was removed by filtration. The diphenyl disulfide was recrystallized from ethanol, mp 58–61 °C. The mixed melting point with an authentic sample showed no depression, and the infrared spectra of the collected material and of authentic diphenyl disulfide were identical. The pentane was evaporated to give a colorless oil which was evaporatively distilled at 3.4×10^{-4} mm at room temperature. About 1.2 g of colorless liquid was collected. The ^{31}P NMR spectrum of this material showed it to be 80% pentaethoxyphosphorane and 20% triethyl phosphate. The ^{1}H and ^{31}P NMR spectra agreed with those previously reported.

Pentaisopropyloxyphosphorane (22). A solution of 1.04 g (0.005 mol) of triisopropyl phosphite in 5 mL of pentane was added dropwise with stirring at −78 °C to a solution of 1.68 g (0.010 mol) of isopropyl benzenesulfenate in 20 mL of pentane which was under a nitrogen atmosphere. After the addition, the white suspension was allowed to warm to room temperature gradually. The ^{31}P NMR spectrum of an aliquot indicated ca. 80% phosphorane, δ +69, with the remainder being phosphate, δ +4. The pentane solution was cooled to −78 °C and filtered with the aid of a filter stick. The filtrate was extracted with four 5-mL portions of propylene carbonate. The pentane layer was evaporated to give an oil whose ^{31}P NMR spectrum indicated at least 95% phorphorane. The ^{1}H NMR spectrum indicated that less than 10% of diphenyl disulfide remained in the sample.

Preparation of Pentaneopentyloxyphosphorane (23). A solution of 3.68 g (0.0188 mol) of neopentyl benzenesulfenate in 10 mL of pentane was added dropwise to a solution of 2.75 g (0.0094 mol) of trineopentyl phosphite in 25 mL of pentane. The reaction mixture was stirred and maintained at −78 °C during the addition. After stirring at −78 ° for 2 h, the reaction mixture was allowed to warm to room temperature. It was concentrated to 25 mL and extracted with five 25-mL portions of propylene carbonate. The pentane was removed to give a white solid, mp 79–80 °C. The spectral properties are recorded in Table I.

Preparation of Pentacyclopentyloxyphosphorane (24). To a solution of 0.364 g (0.00127 mol) of tricyclopentyl phosphite in a few milliliters of methylene chloride was added with stirring at −78 °C a solution of cyclopentyl benzenesulfenate, 0.493g (0.00254 mol) in a few milliliters of methylene chloride. The reaction mixture was allowed to warm to room temperature, and the methylene chloride was removed in vacuo. The residue was dissolved in 10 mL of pentane, and the pentane was extracted with five 10-mL portions of propylene carbonate. Evaporation of the pentane afforded a white solid which decomposed on heating. The spectral data for this material are recorded in Table I.

Preparation of Pentacyclohexyloxyphosphorane (25). To a stirred solution of 2.07 g (0.0063 mol) of tricyclohexyl phosphite in 25 mL of pentane at −78 °C was added a solution of 2.625 g (0.001262 mol) of cyclohexyl benzenesulfenate in 15 mL of pentane over a period of

1 h. After 7 h the mixture was allowed to warm to room temperature, and it was then concentrated to 25 mL and extracted with five 25-mL portions of propylene carbonate. The pentane layer was evaporated to give a white solid, mp 90–92 °C. The spectral properties of this material are reported in Table I.

Preparation of Pentabenzyloxyphosphorane (26). Neither benzyl benzenesulfenate nor tribenzyl phosphite could be distilled without decomposition. These materials were prepared in the usual manner and used as obtained. Their spectral properties are recorded in Table I.

A solution of 0.216 g (0.001 mol) of benzyl benzenesulfenate in a few milliliters of carbon tetrachloride was added at 0 °C to a solution of 0.176 g (0.0005 mol) of tribenzylphosphite in a few milliliters of carbon tetrachloride. The ^{31}P NMR spectrum of the reaction mixture 30 min after mixing showed two major absorptions in a 1:1 ratio at δ 0 and +69. The first absorption is due to phosphite and the second is due to phosphorane. After 3 days the phosphorane had completely decomposed.

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Reaction of 1,4-Diiodonorbornane, 1,4-Diiodobicyclo[2.2.2]octane, and 1,5-Diiodobicyclo[3.2.1]octane with Butyllithium. Convenient Preparative Routes to the [2.2.2]- and [3.2.1]Propellanes[1]

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Abstract: The reactions of 1,4-diiodobicyclo[2.2.2]octane and 1,5-diiodobicyclo[3.2.1]octane with *tert*-butyllithium provide convenient synthetic routes to the [2.2.2]- and [3.2.1]propellanes. The corresponding reaction of 1,4-diiodonorbornane gave 1-*tert*-butyl-4-iodonorbornane as a major product. Whereas 1,4-dibromonorbornane did not react with *tert*-butyllithium, 1-bromo-4-iodonorbornane did react and again gave 1-*tert*-butyl-4-iodonorbornane. The replacement of bromine rather than iodine indicates that both halogens are involved in the reaction and suggests that the [2.2.1]propellane may be an intermediate.

The intriguing properties of small-ring propellanes,[3] a class of compounds in which all four bonds to a carbon atom are constrained to lie on one side of a plane, have stimulated considerable synthetic and theoretical interest. Although elegant synthetic approaches to a number of small-ring propellanes have been reported,[3] most syntheses are limited in that they are not generally applicable to the synthesis of other highly strained propellanes. For this reason, we have been investigating routes to this class of tricyclic hydrocarbons which involve reduction of a suitably bridgehead–bridgehead disubstituted bicyclic hydrocarbon. Our initial goal was the preparation of the elusive [2.2.1]propellane[5] (**1**).

Whereas the electrochemical reduction of 1,5-dibromobicyclo[3.2.1]octane[6] and 1,4-dibromobicyclo[2.2.2]octane[7] led to the formation of the corresponding propellanes, the analogous reduction of 1,4-dibromonorbornane failed to give the [2.2.1]propellane (**1**) or any monomeric product which could unambiguously be attributed to the intermediacy of the [2.2.1]propellane.[8] In a search for other methods by which the conversion might be effected, the reaction of bridgehead–