

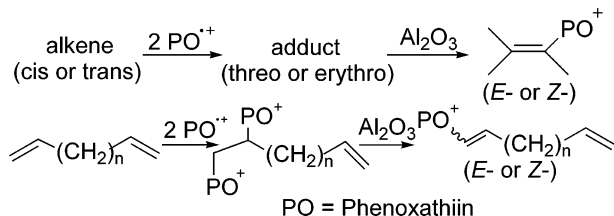
Addition of the Phenoxathiin Cation Radical to Alkenes and Nonconjugated Dienes. Formation of (*E*)- and (*Z*)-(10-Phenoxathiiniumyl)alkenes and (*E*)- and (*Z*)-(10-Phenoxathiiniumyl)dienes on Basic Alumina

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Addition of phenoxathiin cation radical (PO^+) to acyclic alkenes in acetonitrile (MeCN) solution occurred stereospecifically to form bis(10-phenoxathiiniumyl)alkane adducts. Stereospecific *trans* addition is ascribed to the intermediacy of an episulfonium cation radical. The alkenes used were *cis*- and *trans*-2-butene, *cis*- and *trans*-2-pentene, *cis*- and *trans*-4-methyl-2-pentene, *cis*- and *trans*-4-octene, *trans*-3-hexene, *trans*-3-octene, *trans*-5-decene, *cis*-2-hexene, and *cis*-2-heptene. The *erythro* bisadducts (compounds **6**) were obtained with *trans*-alkenes, while *threo* bisadducts (compounds **7**) were obtained with *cis*-alkenes. The assigned structures of **6** and **7** were consistent with their NMR spectra and, in one case, **6c** (the adduct of *trans*-4-methyl-2-pentene) was confirmed with X-ray crystallography. Additions of PO^+ to 1,4-hexa-, 1,5-hexa-, 1,6-hepta-, and 1,7-octadiene gave bis(10-phenoxathiiniumyl)alkenes (compounds **8**), the assigned structures of which were consistent with their NMR spectra. Each of these adducts lost a proton and phenoxathiin (PO) when treated with basic alumina in MeCN solution. Compounds **6** (from *trans*-alkenes) gave mixtures of (*Z*)- (**9**) and (*E*)-(10-phenoxathiiniumyl)alkenes (**10**) in which the (*Z*)-isomers (**9**) were dominant. On the other hand, compounds **7** (from *cis*-alkenes) gave mixtures of **9** and **10** in which, with one exception (the adduct **7c** of *cis*-4-methyl-2-pentene), compounds **10** were dominant. The path to elimination is discussed. The alkenes **9** and **10** were characterized with NMR spectroscopy and, in one case (**9a**), with X-ray crystallography. Reactions of **8b–d** with basic alumina gave mixtures of (*E*)- (**13**) and (*Z*)-(10-phenoxathiiniumyl)dienes (**14**), in which compounds **13** were dominant. The configuration of the product from **8a** (the adduct of 1,4-hexadiene) could not be settled. Noteworthy features in the coupling patterns and chemical shifts in the NMR spectra of some of the adducts and their products are discussed and related to adduct conformations.

Introduction

Numerous reactions of the thianthrene cation radical (Th^+) have been reported since it was first characterized with ESR spectroscopy.^{1–4} Most of those reactions were with nucleo-

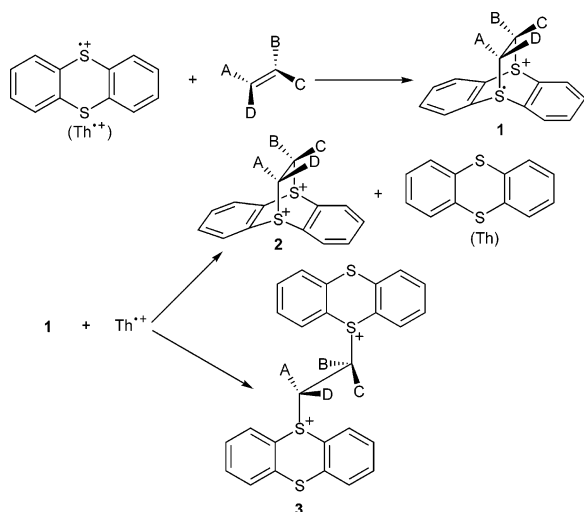
philes and with electron transfer agents.^{5–7} With alkynes^{8,9} and alkenes, however, additions of Th^+ to the unsaturated bonds occur, among which the detailed characteristics of additions to

- (1) Needler, W. C. Ph.D. Dissertation, University of Minnesota, 1961; *Diss. Abstr.* **1962**, 22, 3873.
- (2) Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1962**, 35, 1137–1140.
- (3) Lucken, E. A. C. *J. Chem. Soc.* **1962**, 4963–4965.
- (4) Shine, H. J.; Piette, L. *J. Am. Chem. Soc.* **1962**, 84, 4798–4806.

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SCHEME 1

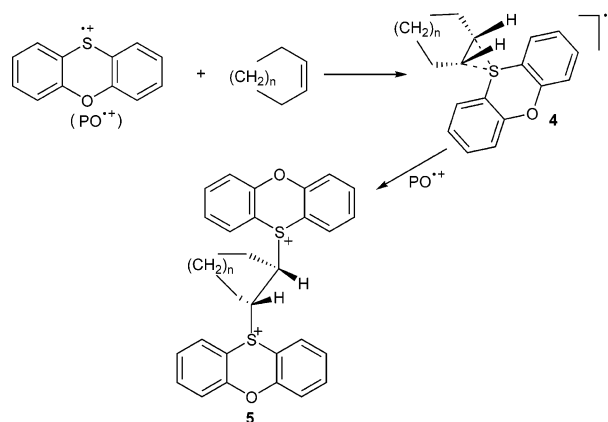


alkenes and cycloalkenes have been established only in more recent years.^{10–16} Two types of adducts are formed, namely, a monoadduct (**2**) having a cyclic structure, and a bisadduct (**3**). They are formed in a way that retains the configuration of the alkene, that is, from a stereospecifically formed cyclic cation radical (**1**), as shown in Scheme 1.

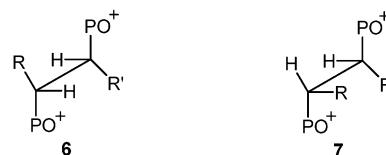
Additions of the phenoxathiin cation radical ($\text{PO}^{\bullet+}$) to alkenes have hitherto not been studied as extensively. Addition to 1-octene to give a bisadduct hydrate was reported more than 25 years ago, without evidence of the adduct's configuration.¹⁷ More recently, addition of $\text{PO}^{\bullet+}$ to some cycloalkenes was accomplished, and the adducts were found to have the *trans* configuration (**5**).¹² Evidence for the participation of a monoadduct analogous to **2** could not be found, and therefore, the stereospecificity of addition was attributed to the involvement of an episulfonium cation radical (**4**, Scheme 2).

We have now carried out reactions of $\text{PO}^{\bullet+}\text{PF}_6^-$ with 13 acyclic alkenes and have isolated their bisadducts. The adducts are numbered **6a–g** for *trans*-alkenes and **7a–c,f,h,i** for *cis*-alkenes. We have also isolated the bisadducts of four nonconjugated dienes. The reactions with dienes were carried out with a large excess of diene to ensure that addition would occur to only one of each diene's two double bonds. These adducts are

SCHEME 2



SCHEME 3



	6	R	R'		7	R	R'
	a	Me	Me		a	Me	Me
	b	Me	Et		b	Me	Et
	c	Me	<i>i</i> Pr		c	Me	<i>i</i> Pr
	d	Et	Et		f	Pr	Pr
	e	Et	Bu		h	Me	Pr
	f	Pr	Pr		i	Me	Bu
	g	Bu	Bu				

numbered **8a–d**. The reactions of all of these adducts with basic alumina led to (10-phenoxathiiniumyl)alkenes (**9** and **10**) and (10-phenoxathiiniumyl)dienes (**13** and **14**).

Results and Discussion

Additions to Alkenes. Thirteen bisadducts were isolated in yields ranging from 48 to 76%. Their structures (Scheme 3) have been assigned as *erythro* from the *trans*- and *threo* from the *cis*-alkenes, meaning that the configuration of an alkene was retained in its adduct. The assignment of structures was helped with X-ray crystallography of one adduct (**6c**), which showed (Figure S1, Supporting Information) the retention of the alkene's (*trans*-4-methyl-2-pentene) configuration. We were unable to grow crystals of other adducts suitable for X-ray crystallography. The assigned *erythro* and *threo* structures were also consistent with the configurations (*E* or *Z*) of (10-phenoxathiiniumyl)-alkenes obtained from reactions of adducts with basic alumina. These configurations are discussed later.

The NMR spectra of compounds **6** and **7** have elements of uniformity consistent with their structures, except in the aromatic ¹H signals. Even in the adducts of symmetrical alkenes (**6a,d,f,g** and **7a,f**), there was not a uniform pattern of aromatic ¹H signals. Instead, throughout all of the **6** and **7** series of adducts, the aromatic ¹H signals were sets of dd and td varying from one

- (5) Joule, A. J. *Adv. Heterocycl. Chem.* **1990**, *48*, 301–393.
 (6) Glass, R. L. *Top. Curr. Chem.* **1999**, *205*, 1–87.
 (7) Rangappa, P.; Shine, H. J. *J. Sulf. Chem.* **2006**, *27*, 617–664.
 (8) Shine, H. J.; Rangappa, P.; Marx, J. N.; Shelly, D. C.; Ould-Ely, T.; Whitmire, K. H. *J. Org. Chem.* **2005**, *70*, 3877–3883.
 (9) Rangappa, P.; Shine, H. J.; Marx, J. N.; Ould-Ely, T.; Kelly, A. T.; Whitmire, K. H. *J. Org. Chem.* **2005**, *70*, 9764–9770.
 (10) Lee, W. K.; Liu, B.; Park, C. W.; Shine, H. J.; Guzman-Jimenez, I. Y.; Whitmire, K. H. *J. Org. Chem.* **1999**, *64*, 9206–9210.
 (11) Qian, D.-Q.; Shine, H. J.; Guzman-Jimenez, I. Y.; Thurston, J. H.; Whitmire, K. H. *J. Org. Chem.* **2002**, *67*, 4030–4039.
 (12) Shine, H. J.; Zhao, B.-J.; Qian, D.-Q.; Marx, J. N.; Guzman-Jimenez, I. Y.; Thurston, J. H.; Ould-Ely, T.; Whitmire, K. H. *J. Org. Chem.* **2003**, *68*, 8910–8917.
 (13) Shine, H. J.; Zhao, B.-J.; Marx, J. N.; Ould-Ely, T.; Whitmire, K. H. *J. Org. Chem.* **2004**, *69*, 9255–9261.
 (14) Zhao, B.-J.; Shine, H. J.; Marx, J. N.; Kelly, A. T.; Hofmann, C.; Whitmire, K. H. *J. Sulf. Chem.* **2006**, *27*, 127–138.
 (15) Zhao, B.-J.; Shine, H. J.; Marx, J. N.; Kelly, A. T.; Hofmann, C.; Ould-Ely, T.; Whitmire, K. H. *J. Sulf. Chem.* **2006**, *27*, 139–147.
 (16) Zhao, B.-J.; Evans, D. H.; Macías-Ruvalcalba, N. A.; Shine, H. J. *J. Org. Chem.* **2006**, *71*, 3737–3742.
 (17) Shine, H. J.; Bandlerish, B. K.; Mani, S. R.; Padilla, A. G. *J. Org. Chem.* **1979**, *44*, 915–917.

adduct to another in their ways of overlapping. In contrast, the methine proton signals were clearly those of symmetric and unsymmetric adducts. In the former, one signal appeared in the region of 3.4–3.8 ppm for both of the methine protons, while in the latter, there were two methine signals in the region of 3.4–4.0 ppm. The magnitudes of coupling of the methine protons were consistent with the structures of the adducts. It is notable that, in unsymmetrical adducts, where coupling between methine protons is possible, it was found to be either small or too small to be detected.

That is, $J = 2.7$ and 2.9 Hz was found for methine–methine proton coupling in **6b**, and 0.8 Hz in **7c**. In all of the other unsymmetrical adducts, no evidence of coupling between methine protons was found, and the coupling patterns of the methine protons could be attributed to adjacent protons without participation of coupling with a methine partner. This indicates that the dihedral angle between the C–H bonds in those adducts was close to 90° .

Another striking feature was observed in the ^1H NMR spectra of some of the adducts. Anomalous high upfield chemical shifts were observed for particular methyl and methylene protons in *erythro* isomers (from *trans*-alkenes) but not from *threo* isomers (from *cis*-alkenes). The clearest unambiguous examples are in the adducts of *trans*- (**6b**) and *cis*-2-pentene (**7b**). In **6b**, the C-5 methyl protons were at $\delta = 0.46$ ppm, whereas in **7b**, they were at $\delta = 1.16$ ppm. This shows that the C-5 methyl group in **6b** is more shielded than that in **7b** by the aromatic ring of a nearby PO^+ group. Differences are also seen in the methyl groups of **6c** and **7c**. In the spectrum of each adduct, there are three methyl group doublets. Those in **6c** were at $\delta = 0.16, 0.97,$ and 1.67 ppm, while those in **7c** were at $\delta = 0.98, 1.29,$ and 1.59 ppm. The shift (0.16 ppm) of one of the methyl groups in **6c** indicates a conformation in which shielding of that methyl group is marked. In the absence of COSY data, we cannot unambiguously assign chemical shifts to the three methyl groups. However, on the basis of comparison with assignable chemical shifts of analogous methyl groups in other adducts, we assign in **6c** the shifts at 0.16 and 0.97 ppm to the isopropyl methyls and at 1.67 ppm to the C-1 methyl. Our reasoning is that if the isopropyl group was not restricted in rotation the averaged chemical shift of its methyl groups would be 0.56 ppm, close to the chemical shifts in the (assumed) unconstrained C-5 methyl in **6b** (0.46 ppm) and the C-1 methyl in **6d** (0.55 ppm) and **6e** (0.56 ppm). Further, the chemical shift of the C-1 methyl group in **6c** (1.67 ppm) is similar to that of the C-1 methyl in **6a** (1.56 ppm) and **6b** (1.47 ppm). In comparison with **6c**, no methyl group in **7c** was so strongly shielded as that at 0.16 ppm.

Similarly, there are two far-upfield methylene protons in the spectra of **6e** (centered at 0.34 ppm) and **6g** (centered at 0.35 ppm). Again, the particular protons cannot be specified, but no *threo* adduct exhibited this feature. The overall indication is that the two PO^+ groups cause greater shielding of particular protons in *erythro* adducts than in *threo* adducts.

Yet another feature in the ^1H NMR spectra of *erythro* adducts points to conformational properties common to some of those adducts. The spectra of **6e–g** included a symmetrical 8-line ddt (ratio 1:2:2:3:3:2:2:1) at $\delta = 1.60$ – 1.63 ppm. The origin of the multiplet was one proton in each of the propyl groups of **6f** and in the butyl groups of **6e** and **6g**. Our interpretation of coupling is shown with one of the butyl groups of **6g** (Figure 1).

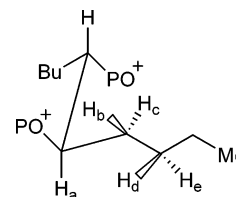
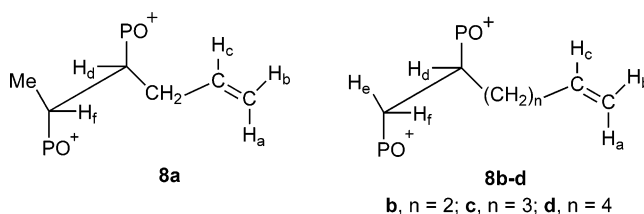


FIGURE 1. Arrangement of protons for coupling with H_b in a butyl group of **6g**.

We attribute the ddt multiplet to H_b , coupling with which occurs from diastereotopic H_c (15 Hz), H_e (10 Hz), H_d (5 Hz), and H_a (5 Hz). The same coupling pattern occurs with the corresponding proton (say, H_b') in the second butyl group, resulting in the observed 2H multiplet. Analogous couplings with H_c (and H_c') should occur, but the NMR signals were not well enough resolved to be deciphered. The multiplet for H_b indicates that a conformation of **6g** must exist in which rotation within the butyl group is restricted. We do not have a definition of that conformation, but it must be one from which pseudo-*cis* elimination of H^+ and PO occurs on alumina to lead to (*Z*)-5- PO^+ -5-decene, as is discussed later.

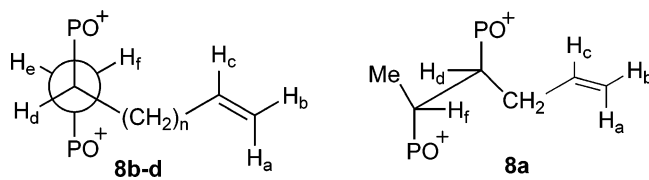
The ^{13}C NMR spectra of **6** and **7** clearly defined the adducts' structures. Thus, the spectrum of each of the six symmetric adducts (**6a,d,f,g** and **7a,f**) showed eight aromatic CH and four aromatic quaternary C atoms, indicating that the two PO^+ units are equivalent but that each itself is not magnetically symmetric. Each of the symmetric adducts had one methine ^{13}C signal. Each ^{13}C spectrum of the seven unsymmetric adducts (**6b,c,e** and **7b,c,h,i**) had 16 aromatic CH and 8 aromatic quaternary C peaks, showing that the two PO^+ units are nonequivalent and magnetically unsymmetric. Correspondingly, each spectrum had two methine C signals. All of the adducts had the expected number of alkyl chain C signals.

Additions to Dienes. The thianthrene cation radical was shown recently to add to one or both of the double bonds of a nonconjugated diene, depending on whether an excess of diene or $\text{Th}^{+\cdot}$ was used.^{14,15} The additions gave complex mixtures of mono-, di(mono)-, bis-, and di(bis)adducts with structures analogous to those of **2** and **3**. In the present work, addition of $\text{PO}^{+\cdot}$ to four dienes was achieved and was less complex than the $\text{Th}^{+\cdot}$ additions. Reactions were carried out using a large excess of diene to ensure addition to only one double bond. Characteristically, only bisadducts (**8a–d**) were obtained, in yields of 36–81%.



8a (from *trans*-1,4-hexadiene) was deduced to have the *erythro* structure on the basis of the expected familiar retention of configuration from addition to a *trans* double bond and of the coupling patterns of the H_d and H_f protons. In each adduct, the pattern of proton–proton coupling among the H_a – H_c and H_d – H_f protons and the ^{13}C NMR spectra were fully consistent with the structures shown. In contrast with the adducts of alkenes (**6** and **7**), coupling between the methine protons of **8a–d** was pronounced. The data are summarized in Table 1. There, a

TABLE 1. NMR Data for Methine Protons in Adducts 8a–d



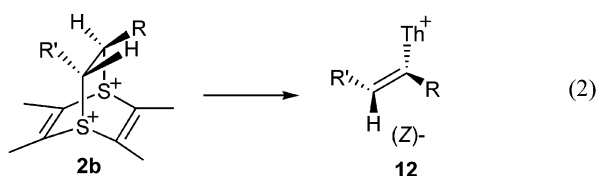
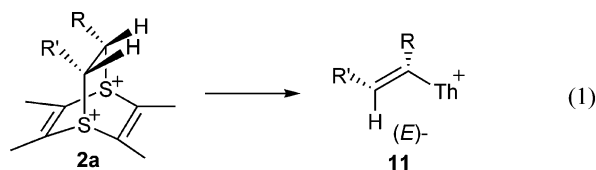
compound	<i>n</i>	δ (ppm) and <i>J</i> (Hz)		
		H _f	H _d	H _e
8a		3.98, qd (6.8, 3.8)	3.77, dt (8.0, 4.3)	1.53, d ^a (7.0)
8b	2	3.72, dd (13.5, 9.0)	3.51, dtd (9.3, 6.4, 3.1)	3.45, dd (13.8, 2.8)
8c	3	3.72, dd (13.5, 9.0)	3.59, dtd (9.0, 6.0, 2.8)	3.43, dd (13.8, 2.8)
8d	4	3.70, dd (13.5, 9.0)	3.59, m –	3.42, dd (14.0, 2.0)

^a CH₃ group.

conformation for **8** is shown that accommodates the coupling constants of protons H_d, H_e, and H_f. With **8b–d**, particularly, the dihedral angles represented in that conformation, namely, 180° for bonds to H_d, H_f and 60° for bonds to H_d, H_e, are diagnostic by the Karplus correlation¹⁸ of coupling constants near to the values of 9 and 2–3 Hz that were observed. Coupling, *J* = 13–14 Hz, between geminal protons H_e and H_f is also recorded in the table.

The coupling parameters of **8a** were not as clearly diagnostic of a conformation as those of **8b–d**. In **8a**, only methine protons H_d and H_f are relevant, and the apparent small coupling constant of 3–4 Hz is diagnostic of a gauche relationship between bonds to those protons. In summary, the NMR data reveal a difference between the conformations of compounds **8** and those of compounds **6** and **7**.

Formation of (*E*)- and (*Z*)-(10-Phenoxathiiniumyl)alkenes from Adducts **6 and **7**. A. Assignment of Configurations.** Recently, we have reported that thianthreniumyl adducts of alkenes¹² and dienes^{14,15} undergo elimination reactions when their solutions are deposited on basic alumina. In the alkene classes, *erythro* monoadducts (e.g., **2a**), made from *cis*-alkenes, gave (*E*)-(5-thianthreniumyl)alkenes (**11**), whereas *threo* monoadducts (e.g., **2b**), made from *trans*-alkenes, gave (*Z*)-(5-thianthreniumyl)alkenes (**12**). The reactions are illustrated with eqs 1 and 2.



More relevant to the present work is the fate of bisadducts. Only two thianthreniumyl bisadducts were isolated in earlier

(18) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; John Wiley: New York, 1998; p 186.

work,¹² owing to the fact that thianthreniumyl bisadducts undergo slow intramolecular conversion into monoadducts, a process that hinders the purification and isolation of bisadducts. The two isolated bisadducts were from *cis*-2-hexene and *cis*-2-heptene. Reaction of the adduct of *cis*-2-hexene (**3a**) with alumina gave a mixture of (*E*)-2-, (*E*)-3-, (*Z*)-2-, and (*Z*)-3-thianthreniumyl-2-hexene, among which the (*Z*)-isomers were dominant. Similarly, reaction of the adduct of *cis*-2-heptene (**3b**) gave a mixture of (*E*)- and (*Z*)-isomers among which the (*Z*)-isomers were again dominant. This is illustrated in Scheme 4 with **3b**, in whose reaction the ratio of (*Z*)- to (*E*)-isomers was 3:1.

The formation of (*E*)-isomers was attributed to pseudo-*cis* elimination, while the dominant formation of (*Z*)-isomers was attributed to anti-periplanar (*app*) eliminations from appropriate conformers. It was noted that the chemical shift of the vinylic proton in (*E*)-isomers was always upfield of the chemical shift of the vinylic proton in (*Z*)-isomers, whether the (5-thianthreniumyl)alkenes were made from monoadducts or the two bisadducts. The difference in chemical shift was attributed to across space shielding of the vinylic proton in (*E*)-isomers by the *cis*-related Th⁺ group. The crystallographic data of one example and the chemical shifts of the vinylic proton in others were factors in assigning (*E*)- or (*Z*)-configuration to the (5-thianthreniumyl)alkenes.

Monoadducts are not obtained in PO⁺ additions. Therefore, we are concerned here only with the behavior of bisadducts **6** and **7**, each of which can, in principle, give an (*E*)- and/or a (*Z*)-(10-phenoxathiiniumyl)alkene (Figure 2).

These compounds are trisubstituted alkenes, and therefore, their configurations cannot be assigned in ¹H NMR spectroscopy by the coupling pattern of the vinylic proton. A configuration *can* be defined, however, with crystallographic information or, in ¹H NMR spectroscopy, by considering the effects of R, R', and PO⁺ on the chemical shift of the vinylic proton. A large amount of data has been assembled in the literature^{19–21} for assigning such configurations. The data have been collated by Lambert^{22a,b} and by Silverstein and Webster.^{22c}

We have deduced that the vinylic protons of (*Z*)-isomers (**9**) have downfield chemical shifts, averaging 6.95 ± 0.06 ppm, and the (*E*)-isomers (**10**) have upfield chemical shifts, averaging 6.53 ± 0.07 ppm. The data are given in Table 2. The reasoning for this deduction is as follows. First, one of the PO⁺-alkenes (**9a**) was defined with X-ray crystallography. The ORTEP diagram (Figure S2, Supporting Information) shows that **9a** has the (*Z*)-2-(10-phenoxathiiniumyl)-2-butene configuration. The chemical shift of its vinylic proton was 7.08. Therefore, (*E*)-2-(10-phenoxathiiniumyl)-2-butene (**10a**), which was made from **7a**, is characterized by its upfield chemical shift, 6.55 ppm.

Next, the controlling influence on δ_H in compounds **9** and **10** was deduced to be the PO⁺ group. That deduction arises from the noted assembly of data in which δ_H is commonly

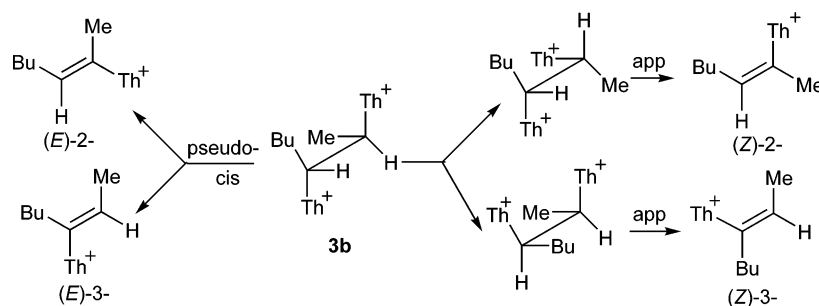
(19) Pascual, C.; Meier, J.; Simon, W. *Helv. Chim. Acta* **1966**, *49*, 164–168.

(20) (a) Matter, U. E.; Pascual, C.; Pretsch, E.; Pross, A.; Simon, W.; Sternhell, S. *Tetrahedron* **1969**, *25*, 691–697; 2023–2034.

(21) Tobey, W. S. *J. Org. Chem.* **1969**, *34*, 1281–1298.

(22) (a) Lambert, J. B. In *Organic Structural Analysis*; Lambert, J. B., Shurvell, H. F., Verbit, L., Cooks, R. G., Stout, G. H., Eds.; MacMillan Publishing Co.: New York, 1976; p 42. (b) Lambert, J. B. In *Organic Structural Spectroscopy*; Lambert, J. B., Shurvell, H. F., Lightner, D. A., Cooks, R. G., Eds.; Prentice Hall: Upper Saddle River, NJ, 1988; p 44. (c) Ref 18, p 206.

SCHEME 4



defined with eq 3.^{19,20a,22} In the PO^+ -alkenes, Z_{gem} is from the alkyl group R and will have the

$$\delta_{\text{H}} = Z_{gem} + Z_{cis} + Z_{trans} \quad (3)$$

same value in (*E*)- and (*Z*)-isomers. The alkyl group R' makes a shielding contribution to δ_{H} that is about the same whether R' is *cis* or *trans* to the vinylic proton. That is, Z_{cis} and Z_{trans} are -0.22 and -0.28 , respectively.^{20a} Therefore, the major influence on δ_{H} must be the PO^+ group. As shown in Table 2, whether in the (*E*)- or (*Z*)-isomer, the vinylic proton is deshielded as compared with ethene itself ($\delta = 5.25$ ppm^{20a}). This results from the distribution of the positive charge of the PO^+ group, shown as $\mathbf{9}^+$ and $\mathbf{10}^+$ in Scheme 5. The difference in the sets of measured δ_{H} in Table 2, then, is attributed to across space shielding of the *cis*-related proton by the PO^+ group in (*E*)-isomers. The same attribution was made earlier with Th^+ -alkenes.¹²

It has not been possible to find a closely related model for shielding in PO^+ -alkenes in the literature. Examples of assignment of configurations of aryl-substituted alkenes are available, however, and they provide support for the PO^+ -alkene assignments. The role of an aromatic group in *Z*-factor assignments can be found in the customary tabulations,^{19,20a,22} and in them, the aromatics appear to be only phenyl and substituted phenyl groups. Among them, Z_{gem} , Z_{cis} , and Z_{trans} are assessed as $+1.38$, $+0.36$, and -0.07 , respectively. The phenyl and substituted phenyl groups in these cases are coplanar with the double bond, so that the *cis*-related proton is in the plane of the aromatic ring and thus in its deshielding zone. In our compounds, the PO^+ group is orthogonal to the double bond, however, as shown in Figure S2 (Supporting Information), and is better modeled by the anthracenyl compounds shown in Scheme 5. Thus, in 9-vinylanthracene,²³ 2-(9-anthracenyl)propene,²⁴ and (*E*)-2-anthracenyl-2-butene,²⁵ the *cis*-related proton is shielded in comparison with its *trans*-related analogue. Abraham has described the anthracenyl group as being orthogonal in 9-vinylanthracene.²³

These examples support our assignment of upfield chemical shifts to (*E*)-isomers and the downfield shift to (*Z*)-isomers, as listed in Table 2.

B. The Stereochemistry of Elimination. Predominantly (*Z*)-isomers (**9**) were made from *erythro* PO^+ adducts (from *trans*-

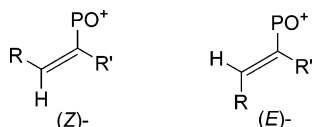


FIGURE 2. (*E*)- and (*Z*)-(10-Phenoxathiiniumyl)alkenes. R and R' are alkyl groups.

alkenes) and (*E*)-isomers (**10**) from *threo* adducts (made from *cis*-alkenes). This is illustrated most easily with adducts (**6a** and **7a**) of a pair of symmetrical *trans*- and *cis*-alkenes, the two 2-butenes, from which only one (*Z*)- or one (*E*)-isomer can be obtained (Scheme 6). Scheme 6 shows that app elimination from **6a** would give (*E*)-2-(10-phenoxathiiniumyl)-2-butene (**10a**), while pseudo-*cis* elimination would give the (*Z*)-2-isomer (**9a**). Experimentally, **6a** gave only **9a**, whose configuration was confirmed with X-ray crystallography (Figure S2, Supporting Information).

Scheme 6 shows also that app elimination from **7a** would give the (*Z*)-isomer (**9a**), while pseudo-*cis* elimination would give the (*E*)-isomer (**10a**). Experimentally, **7a** gave both isomers in the ratio **9a/10a** of 3:7. Thus with both **6a** and **7a** pseudo-*cis* elimination was dominant.

Analogous results were obtained with adducts of other symmetrical alkenes. From **6d** (the adduct of *trans*-3-hexene), the (*Z*)-3- (**9d**) and (*E*)-3-isomer (**10d**) were obtained in the ratio of 95:5. From **6f** (the adduct of *trans*-4-octene), only the (*Z*)-isomer (**9f**) was obtained, while **6g** (from *trans*-5-decene) gave mainly the (*Z*)-5-isomer (**9g**). The *threo* adduct **7f** (from *cis*-4-octene) gave a mixture of (*Z*)-4- (**9f**) and (*E*)-4-isomers (**10f**) in the ratio **9f/10f** of 15:85.

As noted with thianthreniumyl bisadducts of unsymmetrical alkenes,¹² a mixture of four elimination isomers can be formed from each of the PO^+ adducts (**6b,c,e**) and (**7b,c,h,i**) from unsymmetrical alkenes. This made analysis of the NMR spectra of a mixture more complicated, but, nevertheless, often decipherable because only one or two isomers were dominant in a mixture in each case. In most cases, too, the signal from the vinylic proton of even a minor isomer was visible and interpretable, simplifying assignments of configuration. Structural assignments of positional isomers were made on the basis of the chemical shift and coupling of the vinylic proton. An example is given with adducts **6b** (from *trans*-2-pentene) and **7b** (from *cis*-2-pentene).

Reaction of **6b** with alumina gave a mixture of (*Z*)-2- (**9b**) and (*Z*)-3-(10-phenoxathiiniumyl)-2-pentene (**9b'**) in 94% yield and in the ratio **9b/9b'** of 1:2. Signals from (*E*)-isomers were not seen. Reaction of **7b** gave a mixture of two (*E*)- and two (*Z*)-isomers with the ratio *E/Z* of 9:1. The ratio of (*E*)-2-/(*E*)-3-isomers (**10b/10b'**) was 1:2, and the ratio of (*Z*)-2-/(*Z*)-3-isomers (**9b/9b'**) was 4:1.

Thus, with **6b**, the dominant products were (*Z*)-isomers, while with **7b**, they were (*E*)-isomers. These products, then, comply

(23) Abraham, R. J.; Canton, M.; Griffiths, L. *Magn. Reson. Chem.* **2001**, *39*, 421–431.

(24) Coudane, J. *Synthesis* **1981**, 319.

(25) Oki, M.; Taguchi, Y.; Toyota, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2616–2623.

TABLE 2. Chemical Shifts and Coupling Patterns of Alkenyl Protons in (*Z*)- and (*E*)- PO^+ -Alkenes^a

(*Z*-)

compound no.	source	R	R'	(<i>Z</i> -)	δ ppm	coupling pattern (<i>J</i>)
9a^b	6a	Me	Me	2	7.08	qq (7.0, 1.4)
9b	6b	Et	Me	2	7.00	t (8.3)
9b'	6b	Me	Et	3	6.98	q (7.3)
9c	6c	<i>i</i> Pr	Me	2	6.85	dq (10.0, 1.0)
9c'	7c	Me	<i>i</i> Pr	3	6.92	qd (7.4, 1.1)
9d	6d	Et	Et	3	6.89	t (7.5)
9e	6e	Bu	Et	3	6.90 ^c	t (7.5)
9e'	6e	Et	Bu	4	6.90 ^d	t (7.3)
9f	6f	Pr	Pr	4	6.90	t (7.5)
9g	6g	Bu	Bu	5	6.91	t (7.5)
9h	7h	Pr	Me	2	7.02	tq (7.3, 1.3)
9h'	7h	Me	Pr	3	6.99	q (7.3)
9i	7i	Bu	Me	2	7.00	q (7.0)
9i'	7i	Me	Bu	3	6.99	q (7.0)

(*E*-)

compound no.	source	R	R'	(<i>E</i> -)	δ ppm	coupling pattern (<i>J</i>)
10a	7a	Me	Me	2	6.55	qq (7.2, 1.1)
10b	7b	Et	Me	2	6.48	tq (7.9, 1.2)
10b'	7b	Me	Et	3	6.57	qt (7.2, 1.3)
10c	7c	<i>i</i> Pr	Me	2	6.31	dq (10.5, 1.5)
10c'	7c	Me	<i>i</i> Pr	3	6.77	q (7.2)
10f	7f	Pr	Pr	4	6.51	tt (7.8, 1.2)
10g	6g	Bu	Bu	5	6.51	t (7.8)
10h	7h	Pr	Me	2	6.49	tq (7.8, 1.2)
10h'	7h	Me	Pr	3	6.58	qt (7.0, 1.3)
10i	7i	Bu	Me	2	6.49	tq (7.6, 1.0)
10i'	7i	Me	Bu	3	6.58	qt (7.0, 1.0)

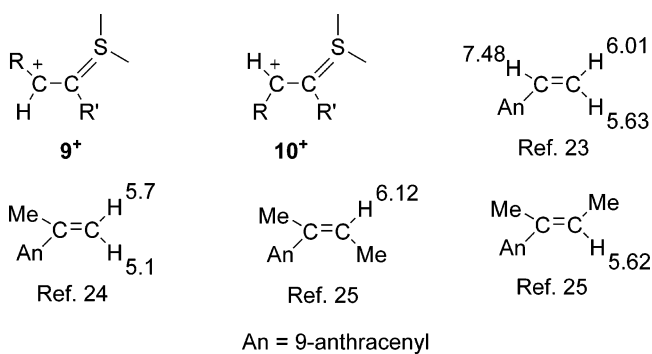
^a All the NMR data are in the Supporting Information. ^b The configuration of **9a** was confirmed with X-ray crystallography. ^c The measured shift was 6.897. ^d The measured shift was 6.901.

with a pseudo-*cis* elimination route, one that differs from the app route observed with the thianthreniumyl bisadducts of *cis*-2-hexene and *cis*-2-heptene.¹²

All of the other PO^+ adducts of unsymmetrical alkenes behaved analogously in reactions with alumina, except the adduct (**7c**) of *cis*-4-methyl-2-pentene. The dominant product of elimination was (*Z*)-3-(10-phenoxathiiniumyl)-4-methyl-2-pentene, formed by app elimination rather than the expected (*E*)-isomer of pseudo-*cis* elimination. This anomalous result may be caused by the especially crowded nature of the conformation required for pseudo-*cis* elimination in this case.

From all of the PO^+ elimination reactions, we have been able to deduce the chemical shifts and couplings of many of the vinylic protons. Often, first-order coupling with adjacent protons and long-range coupling with distant protons were observed. The chemical shifts for the products **9** and **10** and the sources of the products are listed in Table 2.

Formation of (*E*)- and (*Z*)-(10-Phenoxathiiniumyl)dienes from Adducts **8.** Each of the adducts **8a–d** underwent elimination of H^+ and PO in reaction with basic alumina. The

SCHEME 5

eliminations, except that from **8a**, gave (*E*)- (**13**) and (*Z*)-(10-phenoxathiiniumyl)dienes (**14**), whose configurations, unlike those of **9** and **10**, were readily distinguishable by the coupling magnitudes of *cis* and *trans* protons. The NMR data that allowed assignments of configuration of products from **8b–d** are listed in Table 3. These products contain a disubstituted double bond, whereas that from **8a**, 4-(10-phenoxathiiniumyl)-1,4-hexadiene hexafluorophosphate, has a trisubstituted double bond, whose configuration could not be certified. However, the chemical shift of the vinylic proton in **8a** (7.16 ppm) suggests that, by comparison with trisubstituted alkenes **9** and **10**, the (*Z*)-isomer (**14a**) was formed.

From **8a** and **8c**, one major product was obtained along with a very small amount of a second isomer. From **8b**, a mixture of (*E*)- (**13b**) and (*Z*)-1-(10-phenoxathiiniumyl)-1,5-hexadiene (**14b**) was obtained in the ratio of 9:1. From **8d** was obtained a mixture of (*E*)- (**13d**) and (*Z*)-isomers (**14d**) in the ratio of 87:13. The presence of measurable amounts of the minor isomer in the last two cases allowed us to characterize the configuration of both isomers.

Table 3 shows the chemical shifts and couplings of all of the alkenyl protons in the (*E*)-isomers (**13b–d**) and of a number of the alkenyl protons in the (*Z*)-isomers (**14b** and **14d**). Not enough of **14c** was present in the products from **8c** to provide strong enough NMR signals. The difference in coupling constants for H_d (14.5 Hz) and H_d' (8.0 Hz) defines, particularly, the relationship of these protons in the respective isomers. The larger value of *J* defines *trans* protons. A similar pattern of coupling constants was found for the alkene protons in the Th^+ -dienes corresponding to **13** and **14**.^{14,15}

The data in Table 3 show that the H_d protons in (*E*)-isomers are slightly downfield (average $\delta = 7.07 \pm 0.01$ ppm) of the H_d' protons in (*Z*)-isomers (average $\delta = 6.77 \pm 0.11$ ppm). This order in chemical shifts is different from that found with the PO^+ -alkenes, with which δ for the vinylic proton of (*Z*)-isomers (**9**) was larger (av. 6.95) than that (av. 6.53) of (*E*)-isomers (**10**). Possibly, the small, additional downfield shift for the *cis*-related protons in **13b–d** arises from the orientation of the PO^+ group. Its being positioned at the end of the alkenyl chain may allow the group to be oriented in the same plane as the double bond and hence place the *cis*-related proton in the aromatic deshielding zone. Unfortunately, crystals could not be obtained from **13b–d** to provide crystallographic evidence for the PO^+ group's orientation.

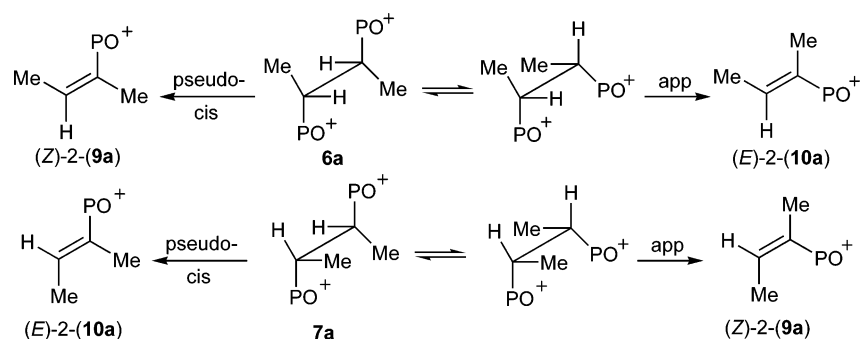
The average chemical shift of the corresponding protons in Th^+ -dienes was 6.85 ± 0.015 ppm for (*E*)- and 6.81 ± 0.013 ppm for (*Z*)-isomers.¹⁴

TABLE 3. Chemical Shifts and Coupling Patterns of Alkenyl Protons in (*E*)- and (*Z*)-PO⁺-Dienes

H	13b <i>n</i> = 2	13c <i>n</i> = 3	13d <i>n</i> = 4	14b <i>n</i> = 2	14d <i>n</i> = 4
d (d')	7.06, dtd (14.5, 7.1, 1.5)	7.08, dt (14.5, 7.1)	7.08, dt (14.5, 7.1)	6.65, q (8.0)	6.88, q (8.0)
e (e')	6.47, dt (14.5, 1.4)	6.47, dt (15.0, 1.5)	6.47, dt (14.5, 1.4)	<i>a</i>	6.43, dt (8.5, 1.4)
c (c')	5.69, ddt (17.0, 10.5, 6.7)	5.73, ddt (17.3, 10.3, 6.7)	5.75, ddt (17.0, 10.5, 6.7)	<i>a</i>	5.87, ddt (17.3, 10.6, 6.6)
a (a')	4.97, dd (17.0, 1.0)	4.92, dq (18.0, 1.4)	4.94, dq (17.3, 1.7)	5.15, (17.3, 1.3)	5.06, dq (17.0, 1.7)
b (b')	4.92, d (10.5)	4.91, dq (9.3, 0.8)	4.90, ddt (10.0, 2.0, 1.0)	5.11, d (10.5)	4.99, ddt

^a Signals from this proton are believed to have been covered by the stronger signals from the (*E*)-isomer.

SCHEME 6



Summary

This work concludes a series of investigations, begun some years ago, of the reactions of two well-known cation radicals, of thianthrene and phenoxathiin, isolable as stable salts, with alkenes and dienes. The investigations began with the serendipitous discovery that in reaction with cyclooctene Th⁺ formed exclusively a new type of cyclic monoadduct (**2**).¹⁰ Thereafter, the formation of both mono- and bisadducts (**3**) from reaction of alkenes and other cycloalkenes was shown to be the general character of additions of Th⁺ salts. The present work now shows that PO⁺ forms only bisadducts in adding to an alkene's double bond. Apparently, the successful bonding to both heteroatoms to form a cyclic adduct in the reactions of Th⁺ is not achievable with the oxygen atom of PO⁺. Nevertheless, additions of PO⁺ are stereospecific, and an episulfonium cation radical (**4**) intermediate is invoked to explain that.

The NMR spectra of the bis(phenoxathiiniumyl) adducts are fully consistent with their structures. The *threo* adducts were formed from *cis*-alkenes, and *erythro* adducts were formed from *trans*-alkenes, consistent with stereocontrolled addition. The NMR spectra of *threo* and *erythro* adducts show interesting differences attributable to differences in configuration and conformational restrictions.

Elimination reactions among bisadducts on basic alumina that were discovered with thianthreniumyl chemistry occurred with phenoxathiiniumyl adducts, too, to give (*E*)- and (*Z*)-PO⁺-alkenes. However, with the latter adducts, pseudo-*cis* elimination prevailed, in contrast with anti-periplanar eliminations in

thianthreniumyl analogues. Consequently, in contrast with thianthreniumyl adducts, *erythro* PO⁺ adducts gave predominantly (*Z*)-isomers and *threo* PO⁺ adducts gave predominantly (*E*)-isomers.

In additions to nonconjugated dienes, controlled in the present work to achieve addition to only one of the double bonds, only bisadducts were formed. That is, formation of di(bis)adducts¹⁵ was avoided. The PO⁺ adducts underwent elimination on basic alumina to form phenoxathiiniumyldienes in analogy to thianthreniumyl adducts that were reported recently.¹⁴

Experimental Section

Phenoxathiin cation radical hexafluorophosphate (PO⁺PF₆⁻) and the procedure for drying solvent MeCN have been described earlier.¹⁰ All alkenes and dienes were from commercial sources. A 500 MHz NMR instrument was used for obtaining all ¹H and ¹³C chemical shifts and coupling data, listed as δ in parts per million and *J* in hertz. Values of *J* have been averaged. CD₃CN was used as NMR solvent in all cases.

Preparation of Bisadducts of Alkenes. A detailed example is given for *erythro*-2,3-bis(10-phenoxathiiniumyl)butane dihexafluorophosphate (**6a**). A solution of 320 mg (5.7 mmol) of *trans*-2-butene in 2 mL of MeCN was added to a stirred suspension of 590 mg (1.70 mmol) of PO⁺PF₆⁻ in 5 mL of MeCN at room temperature. The mixture was stirred overnight (20 h), after which the solution was pink. Dried ether (100 mL) was added dropwise and produced a lot of precipitate, which was filtered and washed with ether to give 260 mg (0.28 mmol, 55%) of product, shown with NMR spectroscopy to be bisadduct (**6a**): mp 130–131 °C (dec); ¹H NMR δ 8.00 (dd, 7.5, 1.5), 7.99 (dd, 7.3, 1.3), 7.97 (dd,

overlapping 4H, 7.5, 1.5), 7.87 (dd, 2H, 8.0, 1.5), 7.71 (td, 8.4, 1.2), 7.69 (dd, overlapping 6H, 8.5, 1.0), 7.64 (dd, 1H, 7.5, 1.0), 7.62 (dd, 1H, 7.5, 1.0), 7.59 (dd, 1H, 7.5, 1.0), 7.57 (dd, 1H, 7.5, 1.0), 3.81–3.74 (m, 2H), 1.56 (d, 6H, 6.0); ^{13}C NMR δ 154.5, 154.1, 139.0, 139.0, 133.3, 133.0, 128.7, 128.6, 121.7, 121.6, 101.1, 97.8, 65.0, 13.8.

threo-2,3-Bis(10-phenoxathiiniumyl)butane Dihexafluorophosphate (7a): mp 147–148 °C (dec), 76%; ^1H NMR δ 7.96 (dd, 1H, 7.3, 1.3), 7.95 (dd, 1H, 7.5, 1.5), 7.91 (dd, 1H, 7.3, 1.3), 7.89 (dd, 1H, 7.3, 1.3), 7.80 (dd, 4H, 8.0, 1.5), 7.63 (dd, 2H, 8.0, 1.0), 7.53 (qd, 4H, 7.8, 1.0), 7.44 (dd, 2H, 8.3, 0.8), 3.70 (q, 7.0), 1.29 (d, 6H, 7.0); ^{13}C δ 153.9, 153.0, 139.1, 138.9, 133.2, 133.1, 128.5, 128.4, 122.0, 121.8, 102.6, 102.2, 60.5, 11.6. Anal. Calcd for $\text{C}_{28}\text{H}_{24}\text{S}_2\text{O}_2\text{P}_2\text{F}_{12}$ (**7a**): C, 45.1; H, 3.24; S, 8.59. Found: C, 45.0; H, 3.46; S, 8.88.

Preparation of (10-Phenoxathiiniumyl)alkenes. An example is given for (Z)-2-(10-phenoxathiiniumyl)-2-butene hexafluorophosphate (**9a**). A solution of 166 mg (0.223 mmol) of **6a** in 6 mL of MeCN was poured onto 40 g of activated alumina held in a fritted glass funnel and was allowed to stand for 1 h. The mixture was washed with MeCN, and the filtrate was evaporated to give a white solid. This was washed three times with ether to remove PO, leaving 84 mg (0.209 mmol) of solid. Assay of a sample with ^1H NMR showed it to be **9a**: mp 177–178 °C, 94%; ^1H NMR δ 7.87 (dd, 7.0, 1.5) and 7.85 (dd, 2H, 7.5, 1.5), 7.80 (dd, 2H, 8.0, 1.5), 7.56 (dd, 8.5, 0.5), 7.54 (dd, 7.5, 0.5), 7.53 (dd, overlapping 4H, 8.3, 0.8), 7.08 (qq, 1H, 7.0, 1.4), 1.90 (dq, 3H, 7.0, 1.0), 1.66 (m, 3H); ^{13}C NMR δ 152.2, 148.5, 137.6, 131.9, 130.6, 128.0, 120.9, 103.3, 16.1, 11.0.

Preparation of Bisadducts of Acyclic Dienes. A detailed example is given for 5,6-bis(10-phenoxathiiniumyl)hexene dihexafluorophosphate (**8b**). To a stirred suspension of 926 mg (2.68 mmol) of PO^+PF_6^- in 8 mL of MeCN was added 1.6 mL (13.5 mmol) of 1,5-hexadiene. After stirring overnight, dry ether was added dropwise giving a precipitate, which was filtered, washed with ether, and dried to give 370 mg (0.48 mmol) of product, shown with NMR spectra to be bisadduct **8b** (36%), mp 123–125 °C (dec). Similar reactions were carried out with *trans*-1,4-hexadiene, 1,6-heptadiene, and 1,7-octadiene, giving **8a**, 51%, mp 97–98 °C (dec); **8c**, 81%, mp 109–110 °C (dec); **8d**, 78%, 108–110 °C (dec).

5,6-Bis(10-phenoxathiiniumyl)hexene dihexafluorophosphate (**8b**): ^1H NMR δ 7.98–7.89 (m, 4H), 7.84–7.81 (m, 3H), 7.72 (dd, 1H, 8.0, 1.5), 7.63 (d, 2H, 8.0), 7.60 (td, 1H, 7.6, 1.0), 7.56 (td, 1H, 7.6, 1.2), 7.54 (d, 8.5), 7.53 (dd, 7.5, 1.0), 7.51 (dd, 7.5, 1.0), 7.50 (dd, overlapping 4H, 8.3, 0.8), 5.67 (ddt, 1H, 17.0, 10.0, 6.5), 5.09 (dq, 1H, 10.3, 1.3), 5.04 (dq, 1H, 17.0, 1.5), 3.72 (dd, 1H, 13.5, 9.5), 3.57 (dtd, 1H, 9.3, 6.3, 3.0), 3.45 (dd, 1H, 13.8, 2.8), 2.72–2.12 (m, 2H), 1.89–1.77 (m, 2H); ^{13}C NMR δ 153.9, 153.8, 153.7, 153.4, 139.1, 139.0, 138.8, 138.7, 136.0, 133.3, 132.8, 132.6, 132.5, 128.9, 128.6 (2CH), 128.4, 122.2, 122.1, 121.8, 121.8, 118.0, 104.2, 103.2, 101.4, 100.1, 60.9, 49.7, 30.1, 29.3.

Preparation of (10-Phenoxathiiniumyl)dienes. An example is given for (*E*)- (**13b**) and (*Z*)-1-(10-phenoxathiiniumyl)-1,5-hexadiene hexafluorophosphate (**14b**). A solution of 180 mg (0.233 mmol) of **8b** in 6 mL of MeCN was poured onto 40 g of activated

alumina held in a fritted glass funnel and was allowed to stand for 1 h. The mixture was washed with MeCN, and the filtrate was evaporated to give a sticky solid. This was washed three times with ether to remove Th, leaving 80 mg (0.188 mmol) of sticky solid. Assay of a sample with ^1H NMR showed it to contain **13b** and **14b** in the ratio of 9:1. The total yield of **13b** and **14b** was 81%.

The reactions of all other diene adducts were carried out in the same way. The following products were isolated. From **8a**: (*Z*)-4-(10-phenoxathiiniumyl)-1,4-hexadiene hexafluorophosphate (**14a**) containing a trace of (*Z*)-5-(10-phenoxathiiniumyl)-1,4-hexadiene hexafluorophosphate (**14a'**), 91%, mp 131–132 °C. The configurations of **14a** and **14a'** could not be assigned with certainty. From **8c**: (*E*)- (**13c**) and (*Z*)-1-(10-phenoxathiiniumyl)-1,6-heptadiene hexafluorophosphate (**14c**), a mixture in the ratio of 97:3, 75%, mp 75–76 °C. From **8d**: (*E*)- (**13d**) and (*Z*)-1-(10-phenoxathiiniumyl)-1,7-octadiene hexafluorophosphate (**14d**), a mixture in the ratio of 87:13, 78%, mp 79–80 °C.

13b: ^1H NMR δ 7.89 (dd, 2H, 8.0, 1.5), 7.86–7.83 (m, 2H), 7.58 (d, 2H, 8.0), 7.53 (t, 2H, 7.5), 7.06 (dtd, 1H, 14.5, 7.1, 1.5), 6.47 (dt, 1H, 14.5, 1.4), 5.69 (ddt, 1H, 17.0, 10.5, 6.7), 4.97 (dd, 1H, 17.0, 1.0), 4.92 (dd, 1H, 10.5), 2.33 (q, 2H, 6.8), 2.16 (q, 2H, 7.0); ^{13}C NMR δ 155.2, 152.1, 137.5, 137.3, 131.8, 127.9, 121.0, 120.6, 116.6, 106.4, 32.4, 31.7.

X-ray Crystallography and Ortep Diagrams. Each single crystal was glued to a glass fiber and mounted on a diffractometer equipped with a CCD area detector. Graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å) in the ω - 2θ scanning mode was used. The data were collected at room temperature and corrected for Lorentz and polarization effects. An absorption correction was applied using the program SADABS. No decay of the crystals was detected during data collection. Heavy atoms in the compounds were located using Patterson methods. The structures were solved using direct methods using the SHELXTL software package and refined by full matrix least-square techniques on F^2 . Hydrogen atoms were included in calculated positions and refined using the riding model. All thermal ellipsoids are drawn at the 50% probability level.

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Supporting Information Available: X-ray crystallographic data for compounds **6c** and **9a** and their Ortep diagrams (Figures S1 and S2); ^1H and ^{13}C NMR data for compounds **6b–6g**, **7b–7i**, **8a,c,d**, **9b–9g**, **10a–10h**, **13c,d**, and **14a**; ^1H expanded NMR spectra and ^{13}C NMR spectra for compounds **6a**, **7a**, **8a**, **9c**, **10f**, and **13c**; products of reaction of **6b–g** and **7b,c,f,h,i** with alumina. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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