139461-46-4; (*i*-PrS)$_3$Si$^{\bullet}$, 139461-47-5; norbornane, 279-23-2; 2-norbornanone, 497-38-1; 1-(methoxycarbonyl)-1-methylcyclopropane, 6206-25-3; adamantane, 281-23-2; cyclohexane, 110-82-7; *N*-ethylmorpholine, 100-74-3; 7-[tris(methylthio)silyl]-Δ^1-*p*-menthene, 139493-26-8; 2-chloronorbornane, 29342-53-8; 3-chloro-2-norbornanone, 61914-03-2; 2,2-dichloro-1-(methoxycarbonyl)-1-methylcyclopropanone, 1447-13-8; 2-bromonorbornane, 29342-65-2; 1-bromoadamantane, 768-90-1; [[(methylthio)thiocarbonyl]oxy]cyclohexane, 41320-40-5; (phenylseleno)cyclohexane, 22233-91-6; (phenylthio)cyclohexane, 7570-92-5; *N*-(2-isocyanoethyl)cyclohexane, 78375-48-1; isocyanocyclohexane, 931-53-3; *β*-pinene, 127-91-3.

Interaction of an Allene with Polyvalent Iodine Derivatives. Preparation, X-ray Molecular Structure, and Some Reactions of Phenyl(2,2-dimethyl-4-(diethylphosphono)-2,5-dihydro-3-furyl)iodonium Salts

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Allene **1** reacts with PhIO/BF$_3$·Et$_2$O or PhIF$_2$/BF$_3$·Et$_2$O in CH$_2$Cl$_2$ at −60 °C with the formation of novel phenyldihydrofuryliodonium salts **2**. Molecular structures for both products **2a**,**b** are determined by X-ray analysis. Iodonium perchlorate **2b** reacts with the anionic nucleophiles (NaN$_3$, NaOCH$_3$, NaOC$_2$H$_5$, CuI/KI) to give the corresponding products of the vinylic nucleophilic substitution (**6a**–**e**) of the iodobenzene moiety. However, analogous reaction of **2b** with Ph$_3$P gives an unexpected iodide **6e** as the major product, along with the usual product of nucleophilic substitution (**6d**). This result is rationalized by a nucleophilic attack of Ph$_3$P on the iodine atom of the iodonium salt **2b** followed by two alternative paths for subsequent ligand coupling.

Introduction

There is widespread current interest in iodonium chemistry.[1] Considerable effort has been devoted to the search for new methods of synthesis, structure investigation, and synthetic application for alkynyl,[2] vinyl,[2c,3,4] and allenylphenyliodonium[2i,5] salts. To date the great majority of the preparations of iodonium salts containing unsaturated moieties are based on the transformation of vinyl and acetylenic derivatives by the action of polyvalent iodine reagents.[2–5] To our knowledge there is only a single example of the reaction of a trivalent iodine reagent, namely [hydroxy(tosyloxy)iodo]benzene, with allenes which, however, proceeds to give ketones and not unsaturated iodonium derivatives.[6] Such reactions may lead to the synthesis of valuable new vinyliodonium compounds and, in the case of substituted allenes, to the question of the regio- and stereoselectivity of these reactions as well as the possible participation of nucleophilic substituents in the final step of addition.

The high leaving-group ability of the phenyliodonio moiety causes instability of vinylphenyliodonium salts under acidic, basic, and neutral conditions.[3a–f] Some of them undergo very facile *β*-elimination yielding the corresponding terminal alkynes.[3a–c,f] Reactions of these salts with nucleophiles allow vinylic nucleophilic substitution with partial or complete inversion of configuration.[3c,f] A

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(1) For reviews see: (a) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. (b) Varvoglis, A. *Synthesis* **1984**, 709. (c) Koser, G. F. In *The Chemistry of Functional groups, Supplement D*; Patai, S.; Rappoport, Z., Eds.; Wiley: New York, 1983; Chapter 25, pp 1265–1351. (d) Moriarty, R. M.; Vaid, R. K. *Synthesis* **1990**, 431. (e) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365. (f) Stang, P. J. *Angew. Chem., Int. Ed. Engl.*, in press.

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(3) (a) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V. *Dokl. Akad. Nauk SSSR* **1971**, *197*, 1337. (b) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Gol'tsev, A. N. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 591. (c) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Lesheva, I. F. *Dokl. Akad. Nauk SSSR* **1978**, *238*, 1109. (d) Ochiai, M.; Kunishima, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095. (e) Ochiai, M.; Oshima, K.; Masaki, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 869. (f) Ochiai, M.; Oshima, K.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, 113, 7059.

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(5) Ochiai, M.; Ito, T.; Takaoka, Y.; Masaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1319.

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Table I. Crystal Data and Details of the Structure Determination of Iodonium Salts 2a and 2b

	2a	**2b**
	(A) Crystal Data	
empirical formula	$C_{16}H_{23}BF_4IO_4P$	$C_{16}H_{23}ClIO_8P$
formula weight	521.5	536.7
crystal system	triclinic	triclinic
space group	$P1$	$P1$
Z	4	2
$F(000)$, electrons	1030	536
a, Å	10.062 (2)	10.599 (2)
b, Å	11.564 (2)	10.609 (2)
c, Å	20.182 (4)	11.510 (2)
α, deg	99.83 (3)	62.88 (2)
β, deg	92.12 (3)	73.25 (2)
γ, deg	109.10 (3)	66.48 (2)
V, Å^3	2174.4 (7)	1047.2 (3)
d_{calc}, Mg/m^3	1.593	1.702
	(B) Data Collection	
diffractometer	Siemens P3/PC	Siemens R3m/V
radiation	MoKα λ = 0.7169 Å	MoKα λ = 0.7169 Å
temp (K)	293	153
2θ range, deg	2.0–52.0	2.0–52.0
scan type	$2\theta - \theta$	$2\theta - \theta$
reflection collected	8645	5133
observed reflections	4880, $F > 8\sigma(F)$	4277, $F > 8\sigma(F)$
	(C) Refinement	
R	0.058	0.039
R_w	0.072	0.044

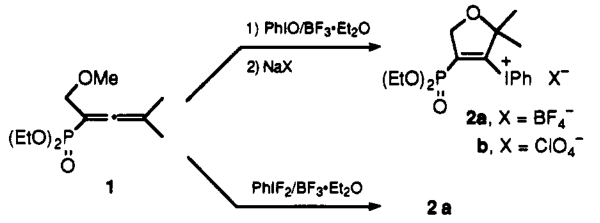
number of mechanisms have been proposed to explain the chemo- and regioselectivity of nucleophilic substitution in vinylphenyliodonium salts. However, little is known about the direction of attack of the nucleophile and about any intermediates formed in these processes. Therefore, further investigation of the reactions of nucleophiles with vinylphenyliodonium salts, especially those containing cycloalkenyl moiety, are desirable.

Hence we wish to report, a mild, one-step preparation of a new type of vinylphenyliodonium salts, **2a**,**b**, by the reaction of the electrophilic iodonium reagents generated from (difluoroiodo)benzene or iodosobenzene and boron trifluoride with the allene **1**[7] and the reactions of these iodonium salts with nucleophilic reagents.

Results and Discussion

Reactions of Allene 1 with Trivalent Iodine Derivatives. It is known that 1,2-alkadienes of type 1 react with halogens,[8] acids,[9] sulfenyl,[10] and selenyl[11] chlorides with the formation of either 1,2-addition products to the double bond or unsaturated heterocyclic compounds due to the participation of the phosphono oxygen atom as an internal nucleophile in the final step of addition. In all these reactions the electrophilic reagent was introduced in a trans fashion to the phosphono substituent.

Scheme I



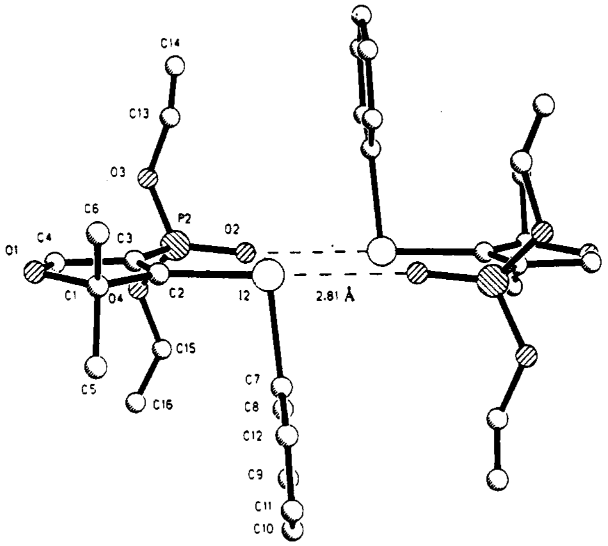


Figure 1. X-ray molecular structure of the dimer of phenyl-(2,2-dimethyl-4-(diethylphosphono)-2,5-dihydro-3-furyl)iodonium ion (**2a**).

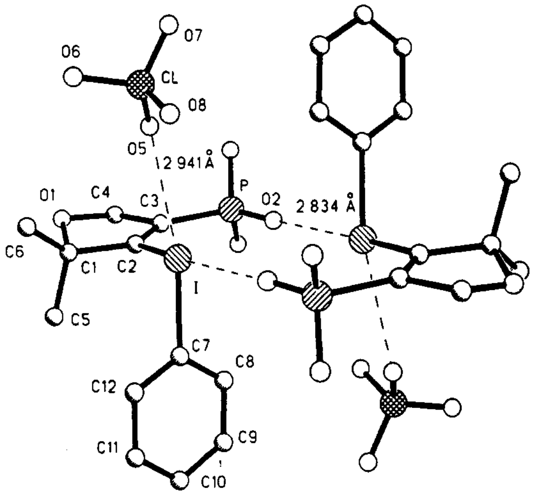


Figure 2. X-ray molecular structure of phenyl(2,2-dimethyl-4-(diethylphosphono)-2,5-dihydro-3-furyl)iodonium perchlorate (**2b**).

The complex of difluoroiodobenzene with boron trifluoride[12] exhibits electrophilic properties and reacts at low temperature with allene **1** to give vinyliodonium salt **2a** in 63% isolated yield. The same compound **2a** was obtained in the reaction of allene **1** with 2 mol equiv of iodosobenzene in the presence of boron trifluoride etherate followed by subsequent treatment of the reaction mixture with an aqueous saturated solution of sodium tetrafluoroborate. If an aqueous solution of lithium perchlorate was used for quenching of the reaction mixture the corresponding perchlorate **2b** was formed in 48% yield.

Both tetrafluoroborate **2a** and perchlorate **2b** are stable, off-white, microcrystalline solids. The structures of both iodonium salts were determined by X-ray analysis. The ^1H, ^{13}C, and ^{31}P NMR spectra are all consistent with the X-ray structural data.

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Table II. Selected Significant Bond Distances (Å) and Bond Angles (deg)[a] for Cations of Iodonium Salts 2a and 2b

	2a	2b
	(A) Bond Distances	
I-C2	2.08 (1)	2.095 (4)
I-C7	2.12 (7)	2.106 (4)
C2-C3	1.34 (2)	1.314 (8)
C3-C4	1.51 (3)	1.521 (6)
C1-C2	1.51 (3)	1.535 (7)
O1-C1	1.44 (2)	1.446 (6)
O1-C4	1.38 (3)	1.42 (1)
P-C3	1.76 (2)	1.801 (6)
	(B) Bond Angles	
C2-I-C7	99.2 (5)	95.8 (2)
I-C2-C3	126 (2)	124.8 (3)
I-C2-C1	121 (1)	122.5 (4)
P-C3-C2	132 (2)	133.4 (3)
P-C3-C4	122 (1)	119.8 (5)
C1-C2-C3	113 (2)	112.5 (4)
O1-C1-C2	102 (2)	100.4 (4)
C1-O1-C4	112 (2)	109.8 (4)
O1-C4-C3	108 (2)	105.1 (5)
C2-C3-C4	106 (2)	106.7 (5)

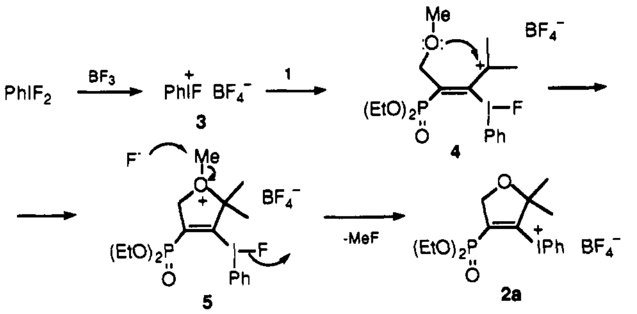
[a] Numbers in parentheses are esd values.

X-ray Structural Data for Iodonium Salts 2a and 2b. Suitable single crystals of **2a** and **2b**, grown from a mixture of chloroform–hexane (1:1), were subjected to standard X-ray analysis (Table I). The molecular geometry of the cations of iodonium salts **2a** and **2b** and the adopted numbering scheme are shown in Figures 1 and 2, respectively. Each structure contains two cations and two anions (tetrafluoroborate in **2a** and perchlorate in **2b**). To clarify the cation structure of **2a** the BF_4^- anions are omitted from the ORTEP diagram in Figure 1. Selected bond distances and angles are listed in Table II; those not mentioned are well within the accepted ranges.

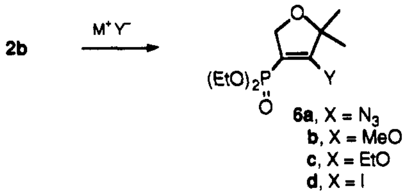
In tetrafluoroborate salt **2a** the dihydrofuran ring is close to planar (in the range 0.02 Å). In the cation of salt **2b** this heterocycle has an envelope conformation in which the O1 atom deviates from the plane C1C2C3C4 by 0.33 Å and the dihedral angle C1–C2–C3–C4 is 2.3°. The same angle in **2b** is 9°. The iodine atom deviates from the plane of the heterocycle by 0.14 Å, whereas the phosphorus atom deviates in the opposite direction by 0.03 Å. As a result the torsion angle I–C2–C3–P is 7° in **2a**.

The two cations form center symmetrical dimers because of hypervalent bonding between the iodine and the oxygen atom of the phosphono group. As a result, salts **2a** and **2b** represent a 10-I-3 polycoordinated iodine species in the Martin–Arduengo formalism.[13] The intermolecular I–O bond distances (2.81 Å in **2a** and 2.83 Å in **2b**) are of the same order as previously observed[3] but significantly less than the sum of the van der Waals radii (3.5 Å) of I–O.[14] Because of the intermolecular bonding between the iodine and P=O oxygen atom each iodine atom has an unusual coordination of the substituents in two different planes. The vinyl carbon and the oxygen atom from a second cation are located in one plane, and the phenyl group is in an orthogonal plane. Coordination around each phosphorus is tetrahedral (in **2a** distorted) with one short (1.44–1.46 Å) and two long P–O bonds (1.55–1.56 Å) and one $P-C_{sp^2}$ bond of 1.76–1.80 Å. All of these bond lengths are within known standard ranges.[15] The other geometrical parameters, including the Ph–I, $I-C_{sp^2}$ and C=C bond lengths as well as the $Ph-I-C_{sp^2}$ and I—C=C bond angles are unexceptional.[3,4] The small values of the torsional angle C2–C3–P–O2 (0° in **2a**, and 2.3° in **2b**) provide evidence for conjugation between C2=C3 and the P=O2 double bonds. It is interesting to emphasize that in both salts each iodine atom is also bonded with one of four fluorine and oxygen atoms from the two tetrafluoroborate (in **2a**) or perchlorate counter anions (in **2b**). The I···F bond distance of 2.85 Å, and the I···O bond of 2.94 Å are very close to the above intermolecular I–O bond distance as previously reported.[16] This value for the I–F distances indicates that the secondary interaction between the iodine and fluorine atoms has some covalent nature with the likely involvement of the d-orbitals of the iodine.

Scheme II



Scheme III



Mechanism of Formation of Iodonium Salts 2a,b. The formation of iodonium salts **2** may be rationalized by the process in Scheme II. Addition of iodonium species **3**, generated from difluoroiodobenzene and boron trifluoride, to allene **1** proceeds highly regioselectively because of the formation of the stabilized allylic carbonium ion **4**. The participation of the methoxy group as a nucleophile at the final step of addition proceeds with loss of methyl fluoride and leads via ring closure to the formation of the observed dihydrofuran iodonium salt **2**.

The course of this reaction is unusual because (i) the electrophilic moiety (PhI^+F) has the *Z* orientation relative to the phosphono substituent in contrast to all previously reported[8-11] preferentional *E* orientation of the substituents at the double bond in the products of the Ad_E reactions of allenes of type **1** and (ii) that a five-membered oxygen-containing heterocyclic iodonium salt is formed since only a few iodonium salts with heterocyclic substituent are known.[18]

Reactions of Iodonium Perchlorate Salt 2b with Nucleophiles. Because processes of vinylic substitution in cycloalkenyl derivatives have unusual features[19] we

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[13] Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Algeria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753. Martin, J. C. *Science (Washington, D.C.)* **1983**, *221*, 509.

[14] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[15] Corbridge, D. E. C. *Studies in Inorganic Chemistry*; Elsevier: New York, 1985; Vol. 6, Phosphorus. P=O 1.46 Å, P—O—C 1.59 Å.

[16] Similar I–F interactions were observed in the 10-oxodibenz[*b*,*e*]iodonium[17a] and diphenyliodonium[17b] tetrafluoroborates; however, in an iodonium ylide no such interactions were reported.[17c]

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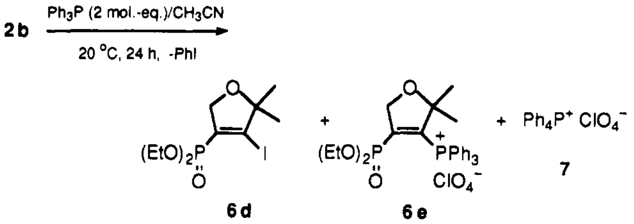
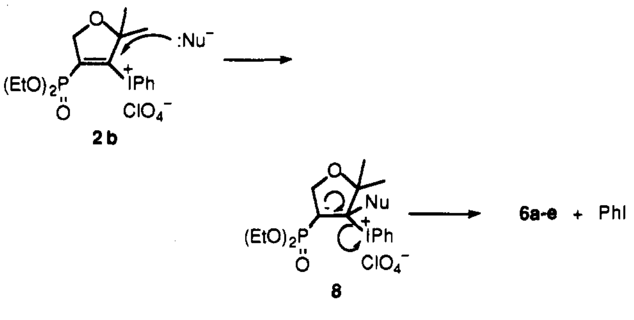
[18] (a) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1985**, *45*, 1542. (b) Carman, C. S.; Koser, G. F. *J. Org. Chem.* **1983**, *48*, 2534. (c) Margida, A. J.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4703.

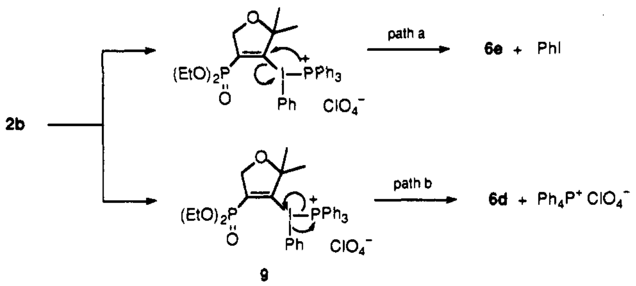
Scheme IV



Scheme V



Scheme VI



decided to carry out some reactions of alkenyl iodonium perchlorate **2b** with different nucleophiles (Scheme III).

The first nucleophilic reagent studied was sodium azide because of the high nucleophilicity of the N_3^- anion. Reaction of perchlorate **2b** with this salt in acetonitrile proceeds very smoothly at room temperature to give the corresponding vinyl azide **6a** with practically quantitative yield (98%). The high reactivity of the vinyliodonium salt was also demonstrated in the reaction with sodium methoxide and ethoxide in alcohol where 3-methoxy **6b** and 3-ethoxy **6c** derivatives were obtained in 83% and 91% yields, respectively. In the reaction of vinyliodonium salt **2b** with CuI/KI in DMFA at room temperature, vinyl iodide **6d** was isolated in high yield (92%).

However, an unexpected reaction occurred on treatment of vinyliodonium salt **2b** with triphenylphosphine in acetonitrile at room temperature, yielding vinyl iodide **6d** and triphenylphosphonium salt **6e** in a 12:5 ratio (68%) along with tetraphenyl phosphonium perchlorate **7** (Scheme IV).

Vinyl derivatives **6a–c** were characterized by ^{1}H and ^{13}C NMR spectra, and for compounds **6a,d,e** the ^{31}P NMR were also obtained.

These data demonstrate the high reactivity of cyclic iodonium salt **2b** with NaN_3, RONa, and CuI/KI in vinylic substitution reactions. To explain the formation of products **6a–d** let us consider first the possibility of an S_N1 mechanism. It is widely recognized[19] that cyclic alkenyl derivatives (especially those containing five- and six-membered rings) are unable to accommodate the linear geometry of a vinyl cation. However, in the solvolysis of 3,3-dimethyl-2-cyclohexenyl triflate, with two methyl groups in the β-position to the leaving group, the products of migration of these substituents were observed[19] and rationalized by the intermediate formation of a vinyl cation. Although vinyliodonium salt **2b** also contains two methyl groups in the β-position to the leaving iodonio moiety no products of skeletal rearrangement were detected, thus likely ruling out the formation of a vinyl cation in the reactions of vinyliodonium salt **2b** with nucleophiles.

In vinylic substitution reactions the Ad–E pathway is the most common[20] and this step-wise approach likely accounts for the formation of products **6a–d** and phosphonium salt **6e** (Scheme V).

Attack of the nucleophile on the sp^2-hybridized carbon atom in the β-position to the leaving iodonium moiety should give intermediate betaine **8**. The presence of the highly electron-withdrawing phosphono group serves as a stabilizing factor and promotes the formation of betaine **8** as the first step. Subsequent elimination of iodobenzene leads to the formation of substitution products **6a–e**. Steric hindrance in the first step, considered to be an important factor in Ad-E processes, is large in iodonium salts **2** where the C-3 atom is shielded by the bulky phosphono group and by the two methyl substituents. Therefore such an Ad-E process may be unfavorable in the reaction of **2b**. Moreover, this mechanism cannot explain the formation of vinyl iodide **6d** in the reaction of iodonium salt **2b** with triphenyl phosphine (Scheme IV).

An alternative possibility is attack of a nucleophile on the iodine atom (Scheme VI) and formation of the transient iodine(III) derivative **9**. Subsequent transformation of intermediate **9** into the products **6d** and **6e** is a consequence of reductive elimination and coupling of various ligands.[21] When iodobenzene is eliminated, ligand coupling of the PPh_3 and the vinyl carbon occurs (path a, Scheme VI). Another type of ligand coupling, namely of phenyl and PPh_3 (path b, Scheme VI), leads to the formation of iodide **6d** as well as the observed tetraphenylphosphonium perchlorate **7**. Although most transformations of phenyliodine(III) derivatives proceed via elimination of iodobenzene in accordance with path a,[1] alternative routes involving ligand coupling are known.[22]

In conclusion, reaction of a PhIO-derived iodine(III) species with a phosphono- and methoxy-substituted allene yields the heterocyclic furanyl iodonium salts **2**. Single-crystal structure determination reveals a novel dimeric 10-I-3 structure in the solid state for **2**. Reaction of **2** with nucleophiles results in the corresponding cyclic adducts **6** whose formation most likely occurs via either a two step Ad-E process and/or attack on iodine, followed by reductive elimination.

Experimental Section

Melting points are uncorrected. ^{1}H and ^{13}C spectral data were obtained at 200 and 50.323 MHz, respectively. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane at 0.00. The ^{31}P NMR spectra were observed at 81.015 MHz, and phosphorus chemical shifts are referenced to 85% H_3PO_4. The ^{19}F NMR was recorded at 188.313 MHz in CD_2Cl_2, and chemical shifts are reported in ppm (δ) relative to $CFCl_3$.

Reaction of Allene 1 with Difluoroiodobenzene in the Presence of Boron Trifluoride Etherate. To a solution of difluoroiodobenzene (0.46 g, 2.7 mmol) in dichloromethane (15 mL) was slowly added boron trifluoride etherate (0.45 g, 3.17

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mmol) at −60 °C, and the mixture was then stirred at this temperature for 30 min. Allene 1 (0.63 g, 2.54 mmol) in dichloromethane (5 mL) was slowly added. The mixture was then allowed to stir at room temperature for 40 min. A 5% aqueous solution of $NaHCO_3$ was added, and the resulting mixture was extracted with chloroform (3 × 10 mL). The combined chloroform fractions were washed with water (20 mL) and dried ($MgSO_4$). Concentration under reduced pressure and crystallization from a mixture of chloroform/hexane (1:1) yielded phenyl(2,2-dimethyl-4-(diethylphosphono)-2,5-dihydro-3-furyl)iodonium tetrafluoroborate (**2a**) (0.83 g, 63%) as a colorless, crystalline solid: mp 118–119 °C; ^1H NMR (CD_2Cl_2) δ 8.20–7.50 (m, 5 H, Ph), 4.84 (d, J = 2.25 Hz, 2 H, CH_2), 4.17 and 4.12 (dq, J = 7.25 Hz, $J_{^{31}P\text{-}H}$ = 8.5 Hz, 4 H, 2 CH_2O), 1.30 (t, J = 7.25 Hz, 6 H, 2 $C\mathit{H}_3CH_2$), 1.26 (s, 6 H, 2 CH_3); ^{13}C NMR (^1H-decoupled, CD_2Cl_2) δ 140.09 (d, C-4), 137.31, 133.97, 132.72, 110.89 (all s, Ph), 127.75 (d, C-3), 93.15 (d, C-2), 74.03 (d, CH_2OP), 64.60 (d, C-5), 26.21 (s, $\mathit{C}H_3C$-2), 16.21 (d, $\mathit{C}H_3CH_2$); ^{31}P NMR (^1H-decoupled, CD_2Cl_2) δ 5.354 (s); ^{19}F NMR (CD_2Cl_2) δ −147.5 (s, BF_4^-). Anal. Calcd for $C_{16}H_{23}BF_4IO_4P$: C, 36.64; H, 4.39. Found: C, 36.58; H, 4.40.

Reactions of Allene 1 with Iodosobenzene and Boron Trifluoride Etherate in the Presence of Salts. To a suspension of iodosobenzene (7.82 g, 35.5 mmol) in dichloromethane (60 mL) was slowly added boron trifluoride etherate (6.2 mL, 50.4 mmol) at −40 °C, and the mixture was then stirred at this temperature for 1.5 h. A solution of allene 1 (4.26 g, 17.2 mmol) in 10 mL of dichloromethane was slowly added. The mixture was stirred at −40 °C for 1 h and then at −10 °C until the suspension dissolved. Stirring was continued for 30 min to warm the mixture to room temperature, and then a saturated aqueous solution of sodium tetrafluoroborate (20 g) or lithium perchlorate trihydrate (28 g) was added. The layers were separated, and the aqueous phase was extracted with chloroform (2 × 20 mL). The combined extracts were dried ($MgSO_4$). Concentration under reduced pressure and crystallization of the residue from a mixture of chloroform/hexane/ether (1:1:2) yielded phenyl(2,2-dimethyl-4-(diethylphosphono)-2,5-dihydro-3-furyl)iodonium tetrafluoroborate (**2a**) (3.85 g, 43%) or phenyl(2,2-dimethyl-4-(diethylphosphono)-2,5-dihydro-3-furyl)iodonium perchlorate (**2b**) (4.42 g, 48%).

For **2b**: mp 139–140 °C dec; ^1H NMR (CD_2Cl_2) δ 8.20–7.30 (m, 5 H, Ph), 4.71 (d, J = 2.25 Hz, 2 H, CH_2), 4.07 and 4.01 (dq, J = 7.25 Hz, 4 H, 2 CH_2O), 1.18 (t, J = 7.25 Hz, 6 H, 2 $C\mathit{H}_3CH_2$), 1.13 (s, 6 H, 2 CH_3); ^{13}C NMR (^1H-decoupled, CD_2Cl_2) δ 141.17 (d, C-4), 137.12, 133.76, 132.01, 11.87 (all s, Ph), 126.27 (d, C-3), 93.41 (d, C-2), 74.27 (d, C-5), 64.59 (d, CH_2OP), 26.27 (s, $\mathit{C}H_3C$-2), 16.33 (d, $\mathit{C}H_3CH_2$). Anal. Calcd for $C_{16}H_{23}ClIO_8P$: C, 35.81; H, 4.32. Found: C, 36.06; H, 4.32.

2,2-Dimethyl-3-azido-4-(diethylphosphono)-2,5-dihydrofuran (6a). A mixture of perchlorate **2b** (0.325 g, 0.61 mmol) and sodium azide (0.351 g, 5.4 mmol) in dry acetonitrile (4 mL) was stirred at room temperature for 1 h. The solvent was distilled off. To the residue was added water (10 mL), and the resulting mixture was extracted with chloroform (3 × 5 mL). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. Column chromatography on silica (hexane and then ethyl acetate/hexane (1:1)) afforded **6a** (0.163 g, 98%) as a bright yellow oil: IR (film) 2128 (N_3), 1258 (P=O), 1047 (PO), 1629 (Ph and C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.64 (d, $^3J_{PCCH}$ = 2.14 Hz, 2 H, CH_2), 4.07 (dq, J = 7.02 Hz, 4 H, 2 CH_2O), 1.34 (s, 6 H, 2 CH_3), 1.30 (t, J = 7.02 Hz, 6 H, $C\mathit{H}_3CH_2$), ^{13}C NMR (^1H-decoupled, $CDCl_3$) δ 152.27 (d, C-4), 109.81 (s, C-3), 86.85 (d, C-2), 72.66 (d, C-5), 61.98 (d, CH_2OP), 25.61 (s, $\mathit{C}H_3C$-2), 16.17 (d, $\mathit{C}H_3CH_2$); ^{31}P NMR (^1H-decoupled, $CDCl_3$) δ 10.83 (s). Anal. Calcd for $C_{10}H_{18}N_3O_4P$: C, 43.64, H, 6.59; P, 11.25. Found: C, 43.92; H, 6.72; P, 11.20.

2,2-Dimethyl-3-methoxy-4-(diethylphosphono)-2,5-dihydrofuran (6b). A mixture of perchlorate **2b** (0.3 g, 0.5 mmol) and sodium methoxide (0.1 g, 2.0 mmol) in methanol (6 mL) was stirred at room temperature for 20 min. After evaporation of methanol in vacuo, water (15 mL) was added. The mixture was extracted with chloroform (3 × 10 mL). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. Column chromatography on silica (ethyl acetate/hexane (1:2)) afforded **6b** (0.123 g, 83%) as a bright yellow oil: ^1H NMR ($CDCl_3$) δ 4.58 (d, $J_{P\text{-}H}$ = 0.6 Hz, 2 H, CH_2), 4.02 (s, 3 H, CH_3O), 3.98 (m, 4 H, 2 CH_2), 1.23 (m, 6 H, 2 $C\mathit{H}_2CH_2$), 1.20 (s, 6 H, 2 CH_3); ^{13}C NMR (^1H-decoupled, $CDCl_3$) δ 169.68 (d, C-4), 119.76 (s, C-3), 86.15 (d, C-2), 72.96 (d, C-5), 61.95 (d, CH_2OP), 60.88 (s, CH_3O), 25.09 (s, CH_3C-2), 16.04 (d, $C\mathit{H}_3CH_2$). Anal. Calcd for $C_{11}H_{21}O_5P$: C, 49.99; H, 8.01. Found: C, 49.86; H, 8.07.

2,2-Dimethyl-3-ethoxy-4-(diethylphosphono)-2,5-dihydrofuran (6c). A mixture of perchlorate **2b** (0.25 g, 0.42 mmol) and sodium ethoxide (0.114 g, 1.68 mmol) in ethyl alcohol (6 mL) was stirred at room temperature for 30 min. Normal workup as described above afforded **6c** (0.106 g, 91%) as a yellow oil: ^1H NMR ($CDCl_3$) δ 4.60 (d, J = 0.6 Hz, 2 H, CH_2), 4.45 (q, 2 H, $OC\mathit{H}_2CH_3$), 4.03 (m, 4 H, $POC\mathit{H}_2CH_3$), 1.25 (m, 6 H, 2 $C\mathit{H}_3CH_2OP$), 1.22 (s, 6 H, 2 CH_3); ^{13}C NMR (^1H-decoupled, $CDCl_3$) δ 169.72 (d, C-4), 118.81 (s, C-3), 86.85 (d, C-2), 73.12 (d, C-5), 25.86 (s, CH_3C-2), 16.08 (d, $\mathit{C}H_3CH_2OP$), 13.09 (s, $COCH_2\mathit{C}H_3$). Anal. Calcd for $C_{12}H_{23}O_5P$: C, 51.79; H, 8.33. Found: C, 51.69; H, 8.40.

2,2-Dimethyl-3-iodo-4-(diethylphosphono)-2,5-dihydrofuran (6d). A mixture of perchlorate **2b** (0.3 g, 0.5 mmol), copper iodide (0.95 g, 5 mmol), and potassium iodide (0.83 g, 5 mmol) in DMFA (10 mL) was stirred at room temperature for 1 h. Concentration under reduced pressure and subsequent chromatography on silica (ethyl acetate/hexane (1:2)) gave iodide **6d** (0.166 g, 92%) as a yellow oil: ^1H NMR ($CDCl_3$) δ 4.68 (s, 2 H, CH_2), 4.15 (dq, 4 H, 2 CH_2O), 1.36 (s, 6 H, 2 CH_3), 1.33 (t, 6 H, $C\mathit{H}_3CH_2$); ^{13}C NMR (^1H-decoupled, $CDCl_3$) δ 132.76 (d, C-4), 114.61 (s, C-3), 93.43 (d, C-2), 76.09 (d, C-5), 62.23 (d, CH_2OP), 25.93 (s, $\mathit{C}H_3C$-2), 16.11 (d, $\mathit{C}H_3CH_2$); ^{31}P NMR (^1H-decoupled, $CDCl_3$) δ 6.86 (s); MS m/z 360.1 (M^+, 0.1), 345 ($M - CH_3$, 100). Anal. Calcd for $C_{10}H_{18}IO_4P$: C, 33.35; H, 5.04; P, 8.60. Found: C, 34.00; H, 5.45; P, 8.08.

Reaction of Perchlorate 2b with Triphenylphosphine. A mixture of perchlorate **2b** (0.234 g, 0.44 mmol) and triphenylphosphine (0.271 g, 1.03 mmol) in acetonitrile (3 mL) was stirred at room temperature for 24 h. Concentration under reduced pressure and subsequent chromatography on silica (ethyl acetate/hexane (1:2 then 1:1) and then acetonitrile) gave iodide **6d** (0.075 g, 48%), perchlorate **6e** (0.052 g, 20%), and tetraphenylphosphonium perchlorate 7 (0.041 g, 22%) as a white crystalline solid.

For **6e**: mp 220–221 °C; ^1H NMR ($CDCl_3$) δ 7.90–7.60 (m, 15 H, 3 Ph), 5.06 (s, 2 H, CH_2), 3.72 (dq, 4 H, 2 CH_2O), 1.16 (s, 6 H, 2 CH_3), 1.10 (t, 6 H, 2 $C\mathit{H}_3CH_2$); ^{13}C NMR (^1H-decoupled, $CDCl_3$) δ 154.90 (d, C-3), 154.60 (d, C-4), 135.26 (s), 134.38 (d) and 130.04 (d, all Ph), 118.29 (d, $C - P^+$), 94.08 (t, C_2), 75.59 (t, C-5), 63.39 (d, CH_2O), 26.61 (s, $\mathit{C}H_3C$-2), 16.05 (d, $\mathit{C}H_3CH_2$); ^{31}P NMR (^1H-decoupled, $CDCl_3$) δ 15.38 (d, J = 10.4 Hz, P=O), 4.26 (d, J = 9.8 Hz, Ph_3P^+). Anal. Calcd for $C_{28}H_{33}ClO_8P_2$: C, 56.62; H, 5.59; P, 10.41. Found: C, 56.90; H, 5.75; P, 10.33.

For **7**: mp 325 °C dec; ^1H NMR (CD_3CN) δ 8.00–7.50 (m, Ph). Anal. Calcd for $C_{24}H_{20}ClO_4P$: C, 65.68; H, 4.59; P, 7.06. Found: C, 65.67; H, 4.59; P, 7.06.

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Supplementary Material Available: Tables of X-ray crystal and structural data for compounds **2a,b** (18 pages). Ordering information is given on any current masthead page.