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Anhydrides of Phosphorus and Sulfur Acids, 2[1]

Mixed Anhydrides of Phosphoric, Phosphonic, and Phosphinic Acids with Sulfonic Acids and Sulfuric Monoimidazolide. New Methods of Synthesis, Novel Structures, Phosphorylating Properties

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New applications of methods leading to anhydrides $RR'P(O)OSO_2R''$ (**1**) are described: a) Reaction of acids $RR'P(O)OH$ (**2**) with sulfonic imidazolides. b) Reaction of phosphorus imidazolides **4** with sulfonic acids and sulfonic anhydrides. New methods of synthesis of anhydrides **1** have been developed. c) Reaction of phosphorus acid silyl esters $RR'P(O)OSiMe_3$ (**9**) with methanesulfonic and trifluoromethanesulfonic anhydrides. d) Reaction of bis(trimethylsilyl) *tert*-butylphosphonate (**10**) with methanesulfonic acid leading to $t\text{BuP(O)(OSO}_2\text{Me)}_2$ (**11**). e) Reaction of stannyl phosphate $(EtO)_2P(O)OSnMe_3$ (**15**) with methanesulfonic anhydride. f) Reaction of phosphorus acid silyl esters **9** with trimethylsilyl trifluoromethanesulfonate. All methods result in high yields and can be adapted to a variety of anhydrides **1** derived from phosphoric, phosphonic, and phosphinic acids on the one hand and methanesulfonic, trifluoromethanesulfonic acids and sulfuric monoimidazolide on the other. Phosphonium intermediates have been demonstrated by low temperature FT ^{31}P NMR spectroscopy for reaction b) and c). The anhydrides **1** are readily converted into imidazolides **4** by the reaction with *N*-(trimethylsilyl)imidazole which proceeds via two distinct phosphonium intermediates. With neutral and weakly basic nucleophiles, the anhydrides **1** behave as phosphorylating agents.

Anhydride aus Säuren des Phosphors und des Schwefels, 2[1]

Gemischte Anhydride von Phosphor-, Phosphon- und Phosphinsäuren mit Sulfonsäuren und Schwefelsäure-monoimidazolid. Neue Synthesen, neue Verbindungen und ihre Eigenschaften als Phosphorylierungsmittel

Es werden neue Anwendungen der Methoden, die zu Anhydriden der Struktur $RR'P(O)OSO_2R''$ (**1**) führen, beschrieben: a) Die Reaktion von Säuren $RR'P(O)OH$ (**2**) mit Sulfonsäure-imidazoliden. b) Die Reaktion von Imidazoliden **4** von Säuren des Phosphors mit Sulfonsäuren und Sulfonsäure-anhydriden. Neue Methoden zur Synthese von Anhydriden der Struktur **1** wurden entwickelt. c) Die Reaktion von Trimethylsilylestern von Säuren des Phosphors $RR'P(O)OSiMe_3$ (**9**) mit Methansulfonsäure- und Trifluormethansulfonsäure-anhydriden. d) Die Reaktion von *tert*-Butylphosphonsäure-bis(trimethylsilylester) (**10**) mit Methansulfonsäure zu $t\text{BuP(O)(OSO}_2\text{Me)}_2$ (**11**). e) Die Reaktion des Stannylphosphats $(EtO)_2P(O)OSnMe_3$ (**15**) mit Methansulfonsäureanhydrid. f) Die Reaktion von Trimethylsilylestern **9** von Säuren des Phosphors mit Trifluormethansulfonsäure-trimethylsilylester. Alle Methoden ergeben hohe Ausbeuten und können an die Vielzahl der Anhydride **1** aus Phosphor-, Phosphon- und Phosphinsäuren einerseits und

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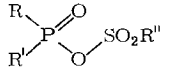
Methansulfonsäure, Trifluormethansulfonsäure und Schwefelsäure-monoimidazolid andererseits angepaßt werden. Für die Reaktionen b) und c) konnten durch Tieftemperatur-FT-^{31}P-NMR-Spektroskopie Phosphonium-Zwischenstufen nachgewiesen werden. Die Anhydride **1** lassen sich durch Umsetzen mit *N*-(Trimethylsilyl)imidazol leicht in Imidazolide **4** überführen; diese Reaktion läuft über zwei verschiedene Phosphonium-Zwischenstufen. Die Anhydride **1** wirken gegenüber neutralen oder schwach basischen Nucleophilen als Phosphorylierungsmittel.

Mixed anhydrides of phosphoric and sulfuric acids are of interest in the biotransfer of sulfates[2]. In the chemical synthesis of oligonucleotides phosphoric sulfonic anhydrides are postulated as reactive intermediates[3]. The anhydrides **1** were recently suggested as intermediates in biooxidation of thiolophosphates[4]. Structural analogues of the anhydrides **1** derived from monothiophosphorus acids have been succesfully used as model for studying the mechanisms and stereochemistry of nucleophilic displacement reactions at the tetracoordinate phosphorus center[5-7].

Satisfactory syntheses of phosphorus sulfonic anhydrides **1** have been reported only recently[1].



1

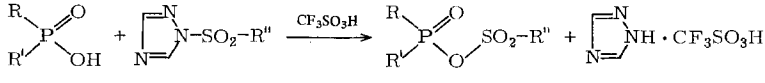
From the point of view of nucleotide and medicinal chemistry it has become of interest to explore the scope of previously described methods for the preparation of **1** and to disclose new routes of potential applicability to the chemistry of phosphorus compounds of biological interest.

In continuation of our previous studies[1] we now report new synthetic and mechanistic aspects of the reaction between phosphorus imidazolides and sulfonic acids or sulfonic anhydrides. We also describe a novel approach to the synthesis of **1** based on phosphorus silyl and stannyl esters.

In the final part of this paper we present new observations on the reactivity of the mixed anhydrides **1** that support our earlier claim that this class of compounds exhibits phosphorylating properties[1]. These also provide new experimental data related to oligonucleotide synthesis by the phosphorotriester methodology promoted by condensing agents such as arenesulfonyl azolides.

Synthesis of Anhydrides 1 via Triazolides of Sulfonic Acids

Trifluoromethanesulfonic acid promoted reaction of phosphorus acids **2** with triazolides **3** of sulfonic acids could be attractive as a direct way of activating the hydroxyl group at the phosphorus atom.



2a-c **3** **1a-c**

	R	R'
2a	*t*Bu	Ph
b	*t*Bu	OMe
c	OEt	OEt

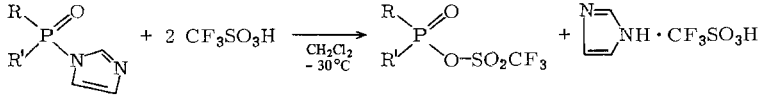
	R	R'	R''	δ^{31}P
1a	*t*Bu	Ph	Me	+56.56
b	*t*Bu	OMe	Me	+33.9
c	OEt	OEt	Me	−13.7

The method is well suited only for the preparation of anhydrides **1** from phosphinic acids like **2a** possessing steric hindrance at the phosphorus center. The synthetic proce-

dure presented above failed, however, to give pure **1** in the case of methyl phosphonate **2b** and diethyl phosphate (**2c**).

Synthesis of Anhydrides 1 via Imidazolides of Phosphorus Acids

The use of phosphorus imidazolides in the synthesis of mixed anhydrides **1** which takes advantage of the lability of the P – N bond in acidic medium[8] has now been extended to the synthesis of mixed anhydrides **1d, e, f** derived from trifluoromethanesulfonic acid.



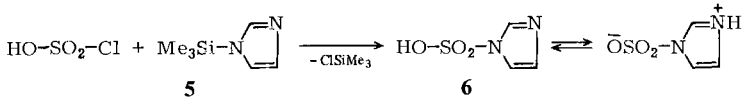
4a-c **1d, e, f**

	R	R'	$\delta^{31}P$
4a	*t*Bu	Ph	40.8
b	*t*Bu	OMe	35.3
c	OEt	OEt	−6.9

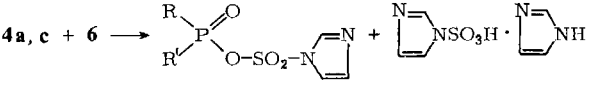
	R	R'	$\delta^{31}P$
1d	*t*Bu	Ph	62.4
e	*t*Bu	OMe	41.0
f	OEt	OEt	−9.46

The anhydrides **1d, e, f** were smoothly formed by allowing the corresponding imidazolides **4** to react with two mol of trifluoromethanesulfonic acid in methylene chloride solution at −30°C. This strongly exothermic reaction was monitored by ^{31}P NMR spectroscopy. Disappearance of **4** and the presence of a single signal corresponding to the anhydride **1d, e, f** showed that the reaction was complete within a few minutes. The anhydrides **1d, e, f** are viscous liquids which decompose on attempted distillation. In addition to the ^{31}P NMR structural data, purity and high yields of **1d, e, f** were demonstrated by converting them into esters RR'P(O)OMe and anilides RR'P(O)NHPh by treating with methanol or aniline, respectively. Both derivatives were formed in high yields and were identical with authentic specimens.

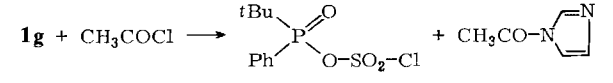
Another synthetic application of the title reaction is shown in the scheme below.



5 **6**

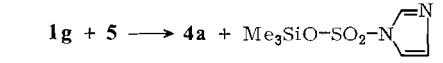


	R	R'	$\delta^{31}P$
1g	*t*Bu	Ph	51.3
h	OEt	OEt	−13.7



1i; $\delta^{31}P = 63.8$

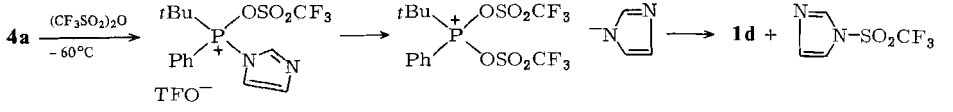
Substitution of chloride in chlorosulfonic acid by the imidazole residue on reaction with 1-(trimethylsilyl)imidazole (**5**) gave sulfuric monoimidazolide (**6**)[9] which reacted with the imidazolides **4a,c** to give the anhydrides **1g,h** in excellent yields. Support for the structure of **1g** comes from acetylation to **1i** obtained also from chlorosulfonic acid. **1i** was converted back into the starting anhydride **1g** on reaction with one mol of **5**. The overall yield was excellent. Reaction of the anhydride **1g** with one mol of **5** gave the imidazolide **4a**, identical with the authentic specimen, in almost quantitative yield.



All reactions mentioned above were monitored by ^{31}P NMR spectroscopy. Our further experience demonstrated that the reaction leading to the imidazolide **4c** can be extended to other types of phosphorus sulfonic anhydrides. This new interesting observation will be described in the chapter dealing with the chemical properties of the anhydrides **1**.

We mentioned in our previous paper[1] that the reaction of imidazolides **4** with sulfonic anhydrides affords mixed anhydrides **1** in good yields under mild conditions in acetonitrile solution.

We have found that this reaction is of wide applicability and, in the case of readily available methanesulfonic anhydride (R″ = Me), can be performed at ambient temperature in methylene chloride solution with almost quantitative yields. The reaction was further extended to trifluoromethanesulfonic anhydride (R″ = CF_3) and *p*-toluenesulfonic anhydride (R″ = *p*-$CH_3C_6H_4$). The exothermic reaction between imidazolides **4** and trifluoromethane sulfonic anhydride proceeds at 0°C in methylene chloride solution in a very clean manner with almost quantitative yields. The structure and purity of the corresponding anhydrides **1d, e, f** and **l** formed was confirmed in the usual way by ^{31}P NMR spectroscopy and by the reactions with an alcohol or aniline. The anhydrides prepared by these methods are of comparable purity to those prepared from the imidazolides **4** and the corresponding sulfonic acids. It was demonstrated by the low temperature ^{31}P NMR spectroscopy that the reaction involves two phosphonium type intermediates. At −80°C two signals were observed at δ = 53.0 and 54.5. The signal at 54.5 disappeared when the temperature of the reaction mixture was raised to −60°C. On that basis we assumed that it can be assigned to salt **8** which decomposes rapidly due to the presence of the strong nucleophile − the imidazolium anion.



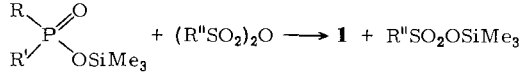
7; $\delta^{31}P = 53.0$ **8**; $\delta^{31}P = 54.5$

The influence of ligands such as the imidazolyl residue on the chemical shift $\delta^{31}P$ of a phosphonium salt is very close to those exercized by a trifluoromethanesulfonyl group.

This will be seen in other sections of this paper. Therefore, on the basis of chemical shifts above it was not possible to distinguish between the two phosphonium salts **7** and **8**.

Synthesis of Anhydrides 1 via Trimethylsilyl Esters of Phosphorus Acids

The trimethylsilyl esters **9** of phosphorus acids can be readily prepared either by silylation of the corresponding acid or of its alkyl esters[10-12]. The silyl group in **9** plays the role of a protecting group since it can be readily removed by hydrolysis, alcoholysis, or attack by fluoride ion. The silyl esters **9** are surprisingly easily converted into mixed anhydrides **1** by reaction with sulfonic anhydrides.

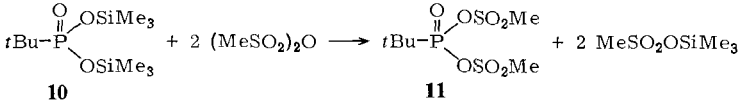


	R	R'
9a	*t*Bu	Ph
b	*t*Bu	OMe
c	OEt	OEt
d	$OSiMe_3$	$OSiMe_3$

	R	R'	R"
1a	*t*Bu	Ph	Me
b	*t*Bu	OMe	Me
c	OEt	OEt	Me
d	*t*Bu	Ph	CF_3

	R	R'	R"
1e	*t*Bu	OMe	CF_3
j	$OSiMe_3$	$OSiMe_3$	Me
k	*t*Bu	Ph	*p*-$CH_3C_6H_4$
l	OEt	OEt	*p*-$CH_3C_6H_4$

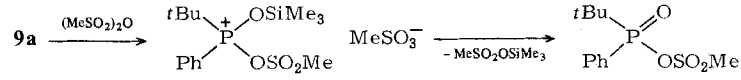
The synthetic value of this "two step" activation of phosphoric acids and their structural analogues is connected with the mild conditions used and high yields of both the silylation reaction and the subsequent reaction with the methanesulfonic anhydride. The latter reaction proceeds at ambient temperature in methylene chloride solution. After removal of solvent and the relatively volatile trimethylsilyl methanesulfonate in vacuo the anhydrides are, in most cases, of high enough purity to be used for further transformations. Several anhydrides **1** including those sterically hindered at phosphorus were prepared by this method. In these cases the identity and purity of **1** was also confirmed either by comparison with specimens prepared by other methods or by phosphorylation of aniline leading to the corresponding anilides. Similarly, starting from disilyl phosphonate **10**, we obtained in good yield and high purity phosphonic sulfonic anhydride **11** containing two residues of methanesulfonic acid.



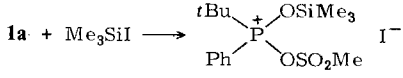
10 **11**

The synthesis of phosphorus sulfonic anhydrides with more then one sulfonic acid residue is being studied in this laboratory.

In order to obtain mechanistic information on the reaction between silyl phosphinates and sulfonic anhydrides we examined the reaction of trimethylsilyl *tert*-butylphenylphosphinate (**9a**) with methanesulfonic anhydride.



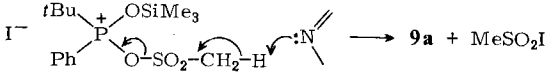
$\delta^{31}P = 40.0$ **12**, $\delta^{31}P = 51.3$ **1a**, $\delta^{31}P = 56.6$



12a, $\delta^{31}P = 52.2$

When both reagents were allowed to react at $-78\,^{\circ}C$ in methylene chloride solution, the phosphonium intermediate **12** was formed (^{31}P NMR) which gradually was converted into the final anhydride **1a** by nucleophilic attack of methanesulfonate anion on the silicon atom. The structure of the phosphonium salt **12** has been confirmed by the formation of the analogous salt **12a** from the anhydride **1a** and trimethylsilyl iodide.

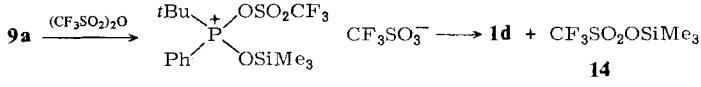
The small difference in chemical shift between **12** and **12a** is not significant and ought to be connected with the fine structure of the ion pairs involved. The structure of **12a** was further supported by its conversion into the starting silyl ester **9a** by action of 2,6-lutidine. This product arises most likely by an elimination reaction and formation of methylenesulfone $H_2C=SO_2$ as an intermediate.



12a

The ability of anhydrides **1** bearing a proton on the carbon atom adjacent to the sulfonyl group to react via methylene sulfone has been established in our previous studies[13,7].

This type of elimination reaction should proceed here even more readily because the phosphorus atom of the phosphonium salt **12a** bears a full positive charge. Formation of the intermediate phosphonium salt **13** was also observed when the silyl ester **9a** was allowed to react with trifluoromethanesulfonic anhydride at $-80\,^{\circ}C$ in methylene chloride solution. The phosphonium salt **13** was transformed slowly into the anhydride **1d**.



13, $\delta^{31}P = 53.5$

The reaction between the silyl ester **9a** and trifluoromethanesulfonic anhydride is, however, restricted in its synthetic applicability. Limitations are connected with strong silylating properties of **14** formed as the second reaction product. For this reason the reaction can only be applied to the preparation of anhydrides derived from trifluoro-

methanesulfonic and phosphinic acids. In case of silyl esters **9b,c** with one or two alkoxy groups attached to phosphorus, a mixture of products is formed because of the transsilylating properties of **14**. The silyl esters derived from phosphinic acids react slowly at ambient temperature with **14**, giving rise to the formation of the anhydride **1d** in 53% yield.

$$\mathbf{9a} + \mathbf{14} \longrightarrow \mathbf{1d} + (Me_3Si)_2O$$

Consequently the reaction of two mol of **9a** with one mol of trifluoromethanesulfonic anhydride lead to the anhydride **1d**.

$$2\,\mathbf{9a} + (CF_3SO_2)_2O \longrightarrow 2\,\mathbf{1d} + (Me_3Si)_2O$$

Synthesis of Anhydrides 1 via Trimethylstannyl Esters of Phosphorus Acids

Trimethylstannyl phosphate **15** is readily available and has been employed for the synthesis of phosphate derivatives of biological interest[14].

We reported an alternative method for the synthesis of anhydride **1c** based on **15** instead of trimethylsilyl analogues: Treatment of trimethylstannyl ester **15** of diethyl phosphate (**2c**) with one equivalent of methanesulfonic anhydride in methylene chloride solution at ambient temperature under strictly anhydrous conditions afforded *O,O*-diethylphosphoric methanesulfonic anhydride (**1c**) in excellent yield as monitored by ^{31}P NMR spectrometry.

$$\underset{\mathbf{15}}{(EtO)_2\overset{\overset{O}{\|}}{P}OSnMe_3} + (MeSO_2)_2O \longrightarrow \mathbf{1c} + MeSO_2OSnMe_3$$

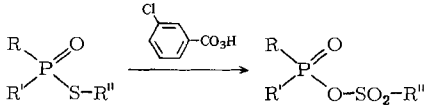
High yield and purity of the anhydride **1c** prepared from **15** is confirmed by conversion of **1c** into diethyl phosphoroanilidate. Evaluation of the scope of the route to anhydrides **1** based on phosphorus acid stannyl esters is in progress.

Reactions of Anhydrides 1 with Nucleophiles and 1-(Trimethylsilyl)imidazole (5)

In our earlier stereochemical studies on the phosphorus sulfonic anhydrides derived from monothioacids of phosphorus ($RR'P(S)OSO_2R''$), we demonstrated their phosphorylating ability towards water and methanol in solvolytic reactions despite of the steric hindrance at the phosphorus center (R = *t*Bu) and the somewhat lower general reactivity of compounds containing the thiophosphoryl group toward nucleophiles in comparison with those containing a phosphoryl group[6,15,16].

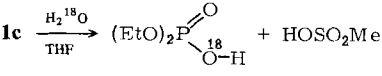
In the previous paper of this series[1] the phosphorylating properties of the anhydrides **1** were demonstrated by quantitative reaction with alcohols and aniline. The reaction with aniline leads to the corresponding anilides $RR'P(O)NHPh$ and provides a good analytical method for evaluation the yield and purity of anhydrides **1** which are difficult to isolate owing to their instability.

In recent publications *Cassida* et al.[4] have suggested that phosphorus sulfonic anhydrides **1** obtained among the spectrum of other products by oxidation of thiophosphates with *m*-chloroperbenzoic acid behave as sulfonating agents.



Among models used by these authors were also compounds which were prepared in this laboratory in pure form by the methods described in this paper. This prompted us to reinvestigate our previous work[1] and to extend its scope. All our previous statements proved to be correct. Esters and amides prepared from a large variety of anhydrides **1** and the corresponding alcohols or primary amines were fully characterized by elemental analysis, comparison with authentic specimens, ^{31}P and ^{1}H NMR data and by mass spectrometry.

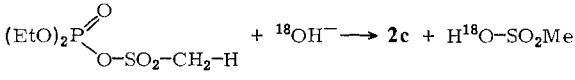
A detailed study of hydrolysis of anhydride **1c** has been carried out using ^{18}O enriched (80%) water in THF solution.



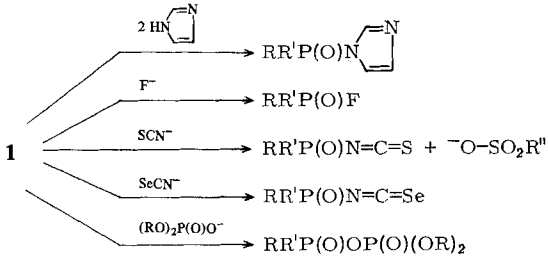
[^{18}O]-**2c**

The diethyl hydrogen phosphate formed had the incorporated ^{18}O atom, which was clearly demonstrated by ^{31}P NMR spectroscopy on the basis of an isotopic effect of 1.941 Hz defined as the difference between resonance signals for the acids with ^{18}O and ^{16}O oxygen atoms[17], respectively. Also the side product tetraethyl pyrophosphate formed by the condensation of **1c** with **2c** exhibited the isotopic effect of 1.459 Hz as a consequence of ^{18}O isotope incorporation.

In contrast the analogous reaction performed with the strongly basic nucleophile ^{18}O-labelled sodium hydroxide led to diethyl hydrogen phosphate without incorporation of this isotope. This was clearly evident from the lack of the isotopic effect in the ^{31}P NMR spectroscopy. The most plausible mechanism for this reaction involves β-elimination leading to $H_2C=SO_2$. The phosphate anion plays the role of leaving group, and no ^{18}O incorporation is expected.



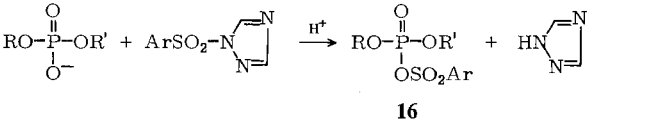
Other nucleophiles such as imidazole, fluoride, thiocyanate, selenocyanate, and dialkyl phosphate anions react readily with anhydrides **1** to yield the corresponding imidazolides, fluoridates, isothiocyanates, isoselenocyanates, and pyrophosphates.



All these nucleophilic displacements took place under mild conditions and led to compounds of high purity in excellent yields.

The results of *Cassida* et al.[4] concerning the sulfonylating properties of the anhydrides **1** were described in preliminary communications and since no experimental data are available we are unable to compare directly our results with those to determine the source of the differences observed.

The phosphoric triester approach plays an important role in the synthesis of oligonucleotides[3]. The formation of an internucleotide linkage is effected by arylsulfonyl azolides as condensing reagents. *Knorre, Zarytova* et al.[3] studied the mechanism of this coupling reaction and postulated the following steps.



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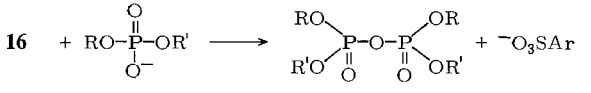

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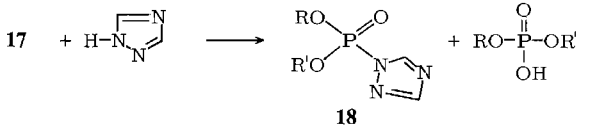
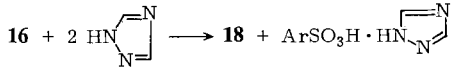


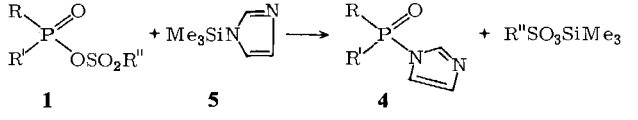
18

Two reactive intermediates, the pyrophosphate **17** and triazolide **18** have been considered as phosphorylating reagents in this system. The latter should be the more powerful phosphorylating reagent due to the leaving group.

Our experimental results showing the facile reaction between the anhydrides **1** and imidazole leading to the corresponding imidazolides emphasize the importance of triazolide **18** as phosphorylating reagent in the phosphorylation promoted by sulfonyl triazolides. The triazolide **18** is likely to be formed not only by the intermediacy of the pyrophosphate **17** but also directly from the intermediate phosphoric sulfonic anhydride **16**.

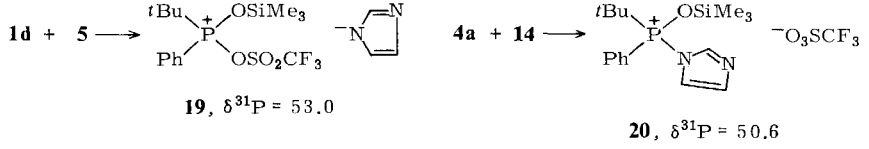


We have developed another method of transforming phosphorus sulfonic anhydrides **1** into the corresponding imidazolides based on the reaction of **1** with 1-(trimethylsilyl)-imidazole (**5**).



1 **5** **4**

The reaction has been successfully carried out with a number of anhydrides **1** at ambient temperature in methylene chloride solution and led to the pure imidazolides in excellent yields. In order to elucidate the mechanistic course of this reaction *tert*-butylphenylphosphinic trifluoromethanesulfonic anhydride (**1d**) was allowed to react with **5** at −60°C. The appearance of two signals $\delta^{31}P$ = 53 and 50.6 were indicative of the formation of the intermediate phosphonium salts **19** and **20**.



19, $\delta^{31}P$ = 53.0

20, $\delta^{31}P$ = 50.6

The phosphonium salt **19**, which is likely to be formed as the primary product, is analogous to salt **13** with $\delta^{31}P$ = 53.3. The signal at $\delta^{31}P$ = 50.6 corresponds to the salt **20** formed after ligand exchange at the phosphorus atom.

We thank the *Polish Academy of Sciences* for support (Research Project MR-I. 12).

Experimental Part

All m. p. are uncorrected. – Solvents and commercial reagents were dried or purified by conventional methods just before use. – NMR spectra: Perkin Elmer R-12 B and Jeol FX 60 Spectrometer, TMS or H_3PO_4 (96%) as standards. – Microanalyses: Microanalysis Laboratory of the Centre of Molecular and Macromolecular Studies, Lodz, Boczna 5. – ^{31}P NMR spectra of ^{18}O labelled compounds: 81 MHz, Bruker WP-005 Y spectrometer, Max-Planck-Institut für Experimentelle Medizin in Göttingen (W. Germany), 85% phosphoric acid as external standard.

Materials: Starting materials and authentic samples such as trimethylsilyl *tert*-butylphenylphosphinate (**9a**)[18], methyl trimethylsilyl *tert*-butylphosphonate (**9b**)[18], diethyl trimethylsilyl phosphate (**9c**)[18], 1-(*tert*-butylphenylphosphinyl)imidazole (**4a**)[1], 1-(diethoxyphosphoryl)-imidazole (**4c**)[1], methanesulfonic anhydride[19], trifluoromethanesulfonic anhydride[20], trimethylsilyl iodide[21], tetraethyl pyrophosphate[18], and diethyl trimethylstannyl phosphate[22] were prepared according to the literature.

Methyl tert-Butylimidazolidophosphonate (**4b**): A solution of **5** (1.54 g, 11 mmol) in 20 ml of dry dichloromethane was added into the stirred solution of methyl *tert*-butylphosphonochloridate (1.71 g, 10 mmol) in 10 ml of dry dichloromethane at 5°C. The solvent, chlorotrimethylsilane formed, and excess of **5** was removed at 25°C/0.01 Torr yielding pure **4b**. Yield 1.99 g (98%); m. p. 125–127°C (THF). – ^1H NMR ($CDCl_3$): δ = 1.2 (d, 9H, J_{PH} = 18.7 Hz), 3.9 (d, 3H, J_{PH} = 120 Hz), 7.5 (s, 2H), 8.2 (s, 1H). – ^{31}P NMR ($CDCl_3$): δ = +35.3.

$C_8H_{15}N_2O_2P$ (202.2) Calcd. C 47.5 H 7.5 N 13.9 P 15.3
Found C 47.3 H 7.4 N 13.8 P 15.2

Methods of Synthesis of Anhydrides **1**

A) *Synthesis of Anhydrides* **1d–f** *via Imidazolides* **4a–c** *of Phosphorus Acids:* To the solution of trifluoromethanesulfonic acid (3.00 g, 20 mmol) in dry CH_2Cl_2 (20 ml) a solution of **4a–c** (10 mmol) in dry ether (20 ml) was added at −30°C. The reaction mixture was stirred 1 h at room temperature. Then the precipitated imidazolium trifluoromethanesulfonate was filtered off. The

solvent was removed in a rotary evaporator. The purity of the resulting anhydrides **1d–f** was determined by ^{31}P NMR (see Table 1). These compounds decompose on attempted distillation at reduced pressure (0.05 Torr), nevertheless, they are stable at room temperature for several hours.

Anhydrides **1g,h** were prepared as described above using 1-imidazolesulfonic acid (**6**)[9], instead of trifluoromethanesulfonic acid. Anhydride **1i** was prepared using **1g** and CH_3COCl or in the reaction of **4a** with chlorosulfonic acid. They are oils. These compounds decompose during purification (see Table 1).

Table 1. ^{31}P NMR shift values and yields of synthesized anhydrides **1**

Method	Substrate No	Product No	R	R′	R″	^{31}P NMR [ppm]	Yield[a] [%]
C	**9a**	**1a**	Ph	*t*Bu	CH_3	+56.56[b]	100
C	**9b**	**1b**	MeO	*t*Bu	CH_3	+33.9[b]	100
C	**9c**	**1c**	EtO	EtO	CH_3	−13.7[b]	80
C	**9a**	**1d**	Ph	*t*Bu	CF_3	+65.9[c]	100
C	**9b**	**1e**	*t*Bu	MeO	CF_3	+40.5[c]	81
C	**9a**	**1k**	*t*Bu	Ph	*p*-$CH_3C_6H_4$	+54.9[c]	97
C	**9c**	**1l**	EtO	EtO	*p*-$CH_3C_6H_4$	−15.5[c]	80
C	**9d**	**1j**	Me_3SiO	Me_3SiO	CH_3	−31.5[c]	100
A	**4a**	**1d**				+62.4[c]	100
A	**4b**	**1e**				+41.0[c]	100
A	**4c**	**1f**	EtO	EtO	CF_3	−9.5[c]	100
A	**4a**	**1g**	*t*Bu	Ph	1-imidazolyl	+51.3[d]	100
A	**4c**	**1h**	EtO	EtO	1-imidazolyl	−13.7[d]	100
A	**4a**	**1i**	*t*Bu	Ph	Cl	+63.8[c]	97
B	**4a**	**1d**				+66.68[c]	100
B	**4b**	**1e**				+40.9[c]	100
B	**4c**	**1f**				−10.8[c]	100
B	**4a**	**1k**				+54.9[c]	100
B	**4c**	**1l**				−14.1[c]	100
D	**9a**	**1d**				+61.3[c]	53
D	**9b**	**1e**				+41.0[c]	47

[a] Estimated by ^{31}P NMR spectroscopy. – [b] In acetonitrile. – [c] In CH_2Cl_2. – [d] In acetone.

tert-Butylphenylphosphinic Trifluoromethanesulfonic Anhydride (**1d**): Yield 100% (by ^{31}P NMR spectroscopy), oil. – ^1H NMR ($CDCl_3$): δ = 1.5 (d, 9H, *t*Bu, J_{PCCH} = 18 Hz), 7.6–8.7 (m, 5H aromatic).

O-Methyl-tert-butylphosphonic Trifluoromethanesulfonic Anhydride (**1e**): Yield 100% (by ^{31}P NMR spectroscopy), oil. – ^1H NMR ($CDCl_3$): δ = 1.4 (d, 9H, *t*Bu, J_{PCCH} = 18 Hz), 4.1 (d, 3H, CH_3, J_{POCH_3} = 10 Hz).

O,O′-Diethylphosphoric Trifluoromethanesulfonic Anhydride (**1f**): Yield 100% (by ^{31}P NMR spectroscopy), oil. – ^1H NMR ($CDCl_3$): δ = 1.5–1.9 (t, 6H, CH_3), 4.3–4.8 (m, 4H, CH_2).

tert-Butylphenylphosphinic Imidazolidosulfuric Anhydride (**1g**): Yield 100% (by ^{31}P NMR spectroscopy), oil. – ^1H NMR ($CDCl_3$): δ = 1.7 (d, 9H, *t*Bu, J_{PCCH} = 18 Hz), 7.3–8.7 (m, 8H, aromatic).

O,O′-Diethylphosphoric Imidazolidosulfuric Anhydride (**1h**): Yield 100% (by ^{31}P NMR spectroscopy), oil. – ^1H NMR ($CDCl_3$): δ = 1.3–1.9 (t, 6H, CH_3), 4.2–4.9 (m, 4H, OCH_2), imidazole 7.0 (s, 1H), 7.6 (s, 1H), 8.2 (s, 1H).

tert-Butylphenylphosphinic Chlorosulfonic Anhydride (**1i**): Yield 97% (by ^{31}P NMR spectroscopy), oil. – ^1H NMR ($CDCl_3$): δ = 1.6 (d, 9H, *t*Bu, J_{PCCH} = 18 Hz), 7.0 – 8.2 (m, 5H, aromatic).

B) *Synthesis of Anhydrides* **1d – f** *via Imidazolides* **4a – c** *of Phosphorus Acids and Trifluoromethanesulfonic Anhydride:* A solution of **4a – c** (10 mmol) in anhydrous CH_2Cl_2 (20 ml) was added at 0°C to the solution of trifluoromethanesulfonic anhydride (1.74 g, 10 mmol) in anhydrous CH_2Cl_2 (10 ml). The reaction mixture was stirred 30 min at room temperature. Then the solvent was removed in a rotary evaporator. The trifluoromethanesulfonic imidazolide (b. p. 30°C/0.05 Torr) was evaporated at 0.05 Torr. The purity of the resulting products **1d, e, f** were determined by ^{31}P NMR (see Table 1), yields 100%. Anhydrides **1k** and **l** were prepared accordingly to the method given above, using *p*-toluenesulfonic anhydride (see Table 1).

tert-Butylphenylphosphinic 4-Methylbenzenesulfonic Anhydride (**1k**): Yield 79%, m. p. 124 – 126°C (benzene/hexane). – ^1H NMR ($CDCl_3$): δ = 1.5 (d, 9H, *t*Bu, J_{PCCH} = 18 Hz), 2.8 (s, 3H, CH_3), 7.5 – 8.7 (m, 9H, aromatic). – ^{31}P NMR ($CDCl_3$): δ = 54.0.

O,O'-Diethylphosphoric 4-Methylbenzenesulfonic Anhydride (**1l**): Yield 100% (by ^{31}P NMR spectroscopy), oil. – ^1H NMR ($CDCl_3$): δ = 1.5 – 2.0 (t, 6H, CH_2CH_3), 2.9 (s, 3H, CH_3), 4.4 – 5.1 (m, 4H, OCH_2), 7.5 – 8.5 (m, 4H, aromatic). – ^{31}P NMR ($CDCl_3$): δ = – 10.4.

C) *Synthesis of Anhydrides* **1** *via Trimethylsilyl Esters* **9** *of Phosphorus Acids and Sulfonic Anhydrides:* A solution of **9** (10 mmol) in dry CH_2Cl_2 (20 ml) was added at 0°C to the solution of sulfonic anhydride (10 mmol) in dry CH_2Cl_2 (20 ml). The mixture was stirred 12 h at room temperature. The solvent was removed in a rotary evaporator. The trimethylsilyl sulfonate was also removed under reduced pressure (0.05 Torr).

Trimethylsilyl Methanesulfonate: b. p. 30°C/0.01 Torr.

Trimethylsilyl Trifluoromethanesulfonate: b. p. 20°C/0.01 Torr.

Trimethylsilyl 4-Methylbenzenesulfonate: b. p. 60°C/0.005 Torr.

tert-Butylphenylphosphinic Methanesulfonic Anhydride (**1a**): Yield 92%, m. p. 103 – 105°C (benzene/hexane) (Lit.[1] 102 – 104°C).

Methanesulfonic O-Methyl-tert-butylphosphonic Anhydride (**1b**): Yield 89%, m. p. 63 – 65°C (benzene/hexane). – ^1H NMR ($CDCl_3$): δ = 1.6 (d, 9H, *t*Bu, J_{PCCH} = 17 Hz), 3.8 (s, 3H, CH_3), 4.3 (d, 3H, CH_3O, J_{POCH} = 11 Hz).

1k: Yield 60%, m. p. 125 – 128°C (benzene/hexane) (Lit.[1] 126 – 128°C).

1c – e, k, j: These compounds are oils and decomposed during attempted purification. Nevertheless, they are stable at room temperature for several hours and are identical with products obtained above according to spectral data (see Table 1).

D) *Synthesis of Anhydrides* **1d, e** *via* **9** *and Trimethylsilyl Trifluoromethanesulfonate* (**14**): The solution of **9a** or **b** (10 mmol) in dry CH_2Cl_2 (20 ml) was added at room temperature to the solution of **14** (2.22 g, 10 mmol) in dry CH_2Cl_2 (20 ml). After 48 h of stirring at room temperature the solvent was removed in a rotary evaporator. The hexamethyldisiloxane was also removed, b. p. 20°C/0.01 Torr. Anhydrides **1d, e** decompose during purification (see Table 1).

1d, e: Yields 53 and 47% (by ^{31}P NMR spectroscopy), identical with the products obtained above.

O,O'-Bis(methylsulfonyl)-tert-butylphosphonic Acid (**11**): To the solution of **10** (290.4 g, 10 mmol) in dry CH_2Cl_2 (20 ml) a solution of methanesulfonic anhydride (3.484 g, 20 mmol) in dry CH_2Cl_2 (10 mmol) was added at room temperature. After 12 h of stirring at room temp. the solvent was removed in a rotary evaporator. The trimethylsilyl methanesulfonate was removed

under reduced pressure, b. p. 30°C/0.01 Torr. Yield 2.766 g (94%), oil. – ^{1}H NMR ($CDCl_3$): δ = 1.5 (d, 9H, *t*Bu, J_{PCCH} = 17 Hz), 3.8 (s, 6H, CH_3). – ^{31}P NMR ($CDCl_3$): δ = 25.7.

E) *Synthesis of Anhydride* **1c** *via Dimethyl Trimethylstannyl Phosphate* (**15**): To the solution of **15** (0.316 g, 1.0 mmol) in dry CH_2Cl_2 (1 ml) a solution of methanesulfonic anhydride (0.174 g, 1.0 mmol) in dry CH_2Cl_2 (1 ml) was added at room temperature. After 4 h of stirring at room temp. the ^{31}P NMR spectrum showed that the reaction was complete. The obtained *O,O'-diethyl-phosphoric methanesulfonic anhydride* (**1c**) was identical with that prepared by other methods described in this paper. Yield 100% (by ^{31}P NMR spectroscopy). – ^{31}P NMR ($CDCl_3$): δ = –13.2.

Reaction of **9a** *with Trifluoromethanesulfonic Anhydride:* To the solution of **9a** (0.129 g, 0.5 mmol) in dry CH_2Cl_2 (1 ml), placed in an NMR tube, a solution of trifluoromethanesulfonic anhydride (0.141 g, 0.5 mmol) in dry CH_2Cl_2 (1 ml) was added at –80°C. Initially the ^{31}P NMR spectrum showed two signals at 53.3 and 62.4 ppm which were attributed to the salt **13** and anhydride **1d**, respectively. After warming up the sample to 20°C, ^{31}P NMR spectrum showed only one signal at 62.4 ppm corresponding to **1d**.

Reaction of Anhydride **1d** *with N-(trimethylsilyl)imidazole* (**5**): To the solution of **1d** (0.165 g, 0.5 mmol) in dry CH_2Cl_2 (1 ml), placed in an NMR tube, a solution of **5** (0.07 g, 0.5 mmol) in dry CH_2Cl_2 (1 ml) was added at –80°C. The ^{31}P NMR spectrum recorded at –80°C showed four signals at 66.6, 53.0, 50.6, and 42.0 ppm which were assigned to **1d**, **19**, **20**, and **4a**, respectively. A spectrum recorded at 20°C showed one dominant signal at 41.9 ppm belonging to **4a**.

Reaction of Anhydride **1a** *with Trimethylsilyl Iodide and 2,6-Lutidine:* To the solution of **1a** (0.276 g, 1.0 mmol) in dry CH_2Cl_2 (1.5 ml), placed in an NMR tube, a solution of trimethylsilyl iodide (0.200 g, 1.0 mmol) in dry CH_2Cl_2 was added at 10°C. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. After 2 h the spectrum showed signals at 52.2 ppm (50%, **12a**) and 54.5 ppm (50%). For the next 48 h the composition of the reaction mixture did not change. Then a solution of 2,6-lutidine (0.107 g, 1.0 mmol) in dry CH_2Cl_2 (0.5 ml) was added at 10°C. A ^{31}P NMR spectrum of the mixture showed signals at 40.1 (50%) and 54.3 ppm (50%), which were assigned to trimethylsilyl *tert*-butylphenylphosphinate (**9a**) and **1a**, respectively.

Reaction of Anhydrides **1c, f, h, l** *with Methanol:* Into an excess of anhydrous methanol maintained at 0°C, the anhydride **1c, f, h, l** was added. After 1 h excess methanol was removed under reduced pressure. The resulting reaction product was purified by distillation.

Diethyl Methyl Phosphate[1]: Yield 89%, b. p. 25°C/0.05 Torr. – ^{1}H NMR (neat): δ = 1.5–1.9 (t, 6H, CH_2CH_3), 4.1 (d, 3H, CH_3, J_{POCH_3} = 9 Hz), 4.3–4.7 (m, 4H, CH_2). – ^{31}P NMR (neat): δ = –0.8.

Reaction of Anhydrides **1d** *and* **e** *with Methanol:* Reactions were performed in ^{31}P NMR tubes. Anhydride **1d** (0.5 mmol) in 0.5 ml of dry CH_2Cl_2 was added to anhydrous methanol (1.5 ml). After 24 h the ^{31}P NMR spectrum of the reaction mixture showed two signals which were assigned to anhydride **1** and product.

Methyl tert-Butylphenylphosphonite: From **1d**. – ^{31}P NMR (CH_3OH/CH_2Cl_2): δ = +53.4.

Dimethyl tert-Butylphosphonate: Analogously from **1e**. – ^{31}P NMR (CH_3OH/CH_2Cl_2): δ = +38.7.

Reaction of the Anhydride **1j** *with Methanol:* To the solution of anhydrous methanol (10 mmol) in anhydrous CH_2Cl_2 (10 ml) a solution of **1j** in anhydrous CH_2Cl_2 (10 ml) was added at room temperature. After 1 h the solvent was evaporated and the crude product was distilled under reduced pressure.

Methyl Bis(trimethylsilyl) Phosphate: Yield 90%, b. p. 35°C/0.01 Torr. – ^{31}P NMR (neat): δ = −15.3.

Reaction of Anhydrides **1c–f, h, l** *with Aniline:* A solution of **1c–f, h, l** (10 mmol) in anhydrous benzene (20 ml) was added at 15°C to the solution of anhydrous aniline (20 mmol) in anhydrous benzene (10 ml). The reaction mixture was kept 30 min at room temperature, then the precipitate was filtered off and washed with $CHCl_3$ (2 × 10 ml). Organic solutions were concentrated under reduced pressure yielding *diethyl N-phenylphosphoroamidate*[1], 80%, m. p. 94–95°C (*n*-pentane). – ^{1}H NMR ($CDCl_3$): δ = 1.6–2.2 (t, 6H, CH_3), 4.3–5.1 (m, 4H, CH_2), 7.3–8.1 (m, 5H, aromatic and NH). – ^{31}P NMR ($CDCl_3$): δ = 2.1.

N-Phenyl-tert-butylphenylphosphinamide: Yield 71%, m. p. 124–126°C (benzene/hexane). – ^{1}H NMR ($CDCl_3$): δ = 1.7 (d, 9H, J_{PHCH} = 18 Hz), 7.3–8.5 (m, 10H, aromatic and NH). – ^{31}P NMR ($CDCl_3$): δ = +40.1.

Methyl N-Phenyl-tert-butylphosphonoamidate: Yield 60%, m. p. 90–92°C (benzene/hexane). – ^{1}H NMR ($CDCl_3$): δ = 1.3 (d, 9H, J_{PHCH} = 18.4 Hz), 3.5 (d, 3H, J_{POCH} = 10 Hz), 7.3–8.1 (m, 5H, aromatic and NH). – ^{31}P NMR ($CDCl_3$): δ = +32.3.

Reaction of Anhydride **1j** *with Aniline:* To the solution of **1j** (3.205 g, 10.0 mmol) in dry ether (10 ml) a solution of aniline (1.863 g, 20 mmol) in dry ether (10 ml) was added. After 1 h the precipitated anilinium salt was filtered off and the filtrate was concentrated. The reaction product, *bis(trimethylsilyl) N-phenylamidophosphate*[23] was crystallized from benzene/hexane. Yield 2.897 g (89%), m. p. 139–140°C. – ^{31}P NMR ($CHCl_3$): δ = −16.04.

Reaction of Anhydrides **1a–i, k, l** *with Imidazole:* To the solution of imidazole (1.360 g, 10.0 mmol) in anhydrous acetone (20 ml) a solution of **1a–i, k, l** (5.0 mmol) in anhydrous acetone (20 ml) was added at room temperature. After 1 h the resulting precipitate was removed by filtration and the filtrate was concentrated.

tert-Butylphenylphosphinic Imidazolide[1] (**4a**): Yield 98%, m. p. 134–135°C (benzene/hexane). – ^{31}P NMR ($CDCl_3$): δ = 42.5.

Methyl tert-Butylimidazolidophosphonate (**4b**): Yield 97%, m. p. 125–127°C (THF). – ^{31}P NMR (CD_3CN): δ = 35.26.

Diethyl Imidazolidophosphate[1] (**4c**): Yield 97% (by ^{31}P NMR spectroscopy). – ^{31}P NMR ($CDCl_3$): δ = −6.7.

Reaction of Anhydrides **1a–f** *and* **1i–k** *with N-(trimethylsilyl)imidazole* (**5**): To the solution of **1** (10 mmol) in anhydrous CH_2Cl_2 (20 ml) a solution of **5** (1.402 g, 10 mmol) in anhydrous CH_2Cl_2 (20 ml) was added dropwise under continuous stirring at room temperature. After 30 min of stirring, solvent and trimethylsilyl methanesulfonate were removed under reduced pressure.

4a: Yield 94%, m. p. 134–136°C (benzene/hexane). – ^{31}P NMR ($CDCl_3$): δ = 42.8.

4b: Yield 92%, m. p. 125–127°C (THF). – ^{31}P NMR (CD_3CN): δ = 35.28.

4c: Yield 97%. – ^{31}P NMR ($CDCl_3$): δ = −6.7.

Reaction of Anhydrides **1g** *and* **h** *with* **5**: Reactions were performed in ^{31}P NMR tubes. The identity of obtained **4a** and **c** were confirmed by ^{31}P NMR chemical shifts and by addition of authentic samples to the reaction mixture.

Reaction of Anhydrides **1c** *and* **f** *with Diethyl Triethylammonium Phosphate:* To the solution of the triethylammonium salt of **2c** (2.553 g, 10 mmol) in dry acetone (10 ml) was added at room temp. the solution of **1c** or **f** (10 mmol) in dry acetone (10 ml). After 9 h of stirring the ^{31}P NMR spectrum showed 100% conversion of the anhydrides. After evaporation of the solvent the

residue was dissolved in $CHCl_3$ (20 ml) and washed with water (2 × 5 ml), then the organic solution was dried over magnesium sulfate. Evaporation of the chloroform gave an oily product which was identified as *tetraethyl pyrophosphate.* Yield 92%, b. p. 93–95°C/0.05 Torr. – ^{31}P NMR (neat): δ = –13.4.

tert-Butylphenylphosphinic O,O-Diethylphosphoric Anhydride, $(EtO)_2P(O)-O-P(O)PhtBu$ was prepared from **1c** or **f** and the triethylammonium salt of *tert*-butylphenylphosphinic acid (**2a**) according to the method described above. Yield 89%, b. p. 140–142°C/0.01 Torr. – ^{31}P NMR (neat): δ = 48.2 (d, J_{POP} = 36.621 Hz), –12.03 (d, J_{POP} = 36.62 Hz).

Reaction of Anhydrides **1** *with Ammonium Thiocyanate:* To the suspension of ammonium thiocyanate (0.761 g, 10 mmol) in dry ether (10 ml) a solution of **1a–k** (10 mmol) in dry ether (10 ml) was added at room temperature. The reaction was complete after 12 h. After evaporation of ether, the oily residue was dissolved in $CHCl_3$ (20 ml) and washed with water (2 × 5 ml). The chloroform solution was dried over magnesium sulfate and concentrated. The crude product was purified by distillation.

Diethyl Phosphoroisothiocyanate: Yield 91%, b. p. 58–61°C/0.5 Torr. – ^{31}P NMR (neat): δ = –19.0.

tert-Butylphenylphosphinoyl Isothiocyanate: Yield 87%, b. p. 85–87°C/0.07 Torr. – ^{31}P NMR ($CDCl_3$): δ = 40.1.

Reaction of Anhydrides **1a–k** *with Ammonium Fluoride:* Anhydride **1** (1.0 mmol), ammonium fluoride (0.037 g, 1.0 mmol) and dry acetone (1 ml) were placed in an NMR tube at room temperature. After 12 h ^{31}P NMR spectrum showed that the reaction was complete.

tert-Butylphenylphosphinoyl Fluoride, tBuPhP(O)F: Yield 100%. – ^{31}P NMR (acetonitrile): δ = 66.1 ($J_{P,F}$ = 1043.15 Hz).

Diethyl Phosphorofluoridate, $(EtO)_2P(O)F$: Yield 100%. – ^{31}P NMR (acetonitrile): δ = –9.81 ($J_{P,F}$ = 969.24 Hz).

Reaction of Anhydrides **1a** *and* **d** *with Potassium Selenocyanate* was performed in acetonitrile solution in an NMR tube. The reaction was complete after 1 h. ^{31}P NMR spectrum showed only one product, *tert*-butylphenylphosphinic selenocyanate, at $\delta^{31}P$ = 43.5.

Reaction of Anhydride **1c** *with* $H_2{}^{18}O$: To the solution of **1c** (0.116 g, 0.5 mmol) in dry THF (1 ml) placed in an NMR tube, a solution of $H_2{}^{18}O$ (80%) (0.5 mmol) in dry THF (1 ml) was added at room temperature. The reaction was complete after few min. ^{31}P NMR spectra indicated that ^{18}O was incorporated only in the diethyl phosphate and tetraethyl pyrophosphate which was formed as a secondary product.

^{31}P NMR spectrum of the reaction mixture showed signals at 0.225 and 0.201 ppm, which were assigned to diethyl phosphate (**2c**) and diethyl [^{18}OH]phosphate ([^{18}O]-**2c**), respectively (isotope effect 1.941 Hz).

The second pair of signals at –13.3065 and –13.3245 ppm were assigned to tetraethyl pyrophosphate and ^{18}O labelled tetraethyl pyrophosphate, respectively (isotope effect 1.459 Hz).

Reaction of Anhydride **1c** *with* $Na^{18}OH$: **1c** (0.116 g, 0.5 mmol), anhydrous THF (1.5 ml) and $Na^{18}OH$ (0.210 g, 0.5 mmol) were placed in an NMR tube. After few min the ^{31}P NMR spectrum showed only one signal at –12.9271 ppm, assigned to tetraethyl pyrophosphate. No incorporation of the ^{18}O was demonstrated by comparison with an authentic specimen prepared as described above using NaOH.

Trimethylsilyl Trifluoromethanesulfonate (**14**): A solution of *N*-(trimethylsilyl)imidazole (**5**) (0.757 g, 5.4 mmol) in 20 ml of dry ether was added under vigorous stirring to trifluoromethanesulfonic acid (1.636 g, 10.9 mmol) at 10°C. After 1 h of stirring at room temp. the precipitated imidazolium salt of trifluoromethanesulfonic acid was filtered off. Concentrating of the filtrate gave a crude product which was purified by distillation. Yield 1.152 g (96%), b. p. 39–40°C/13 Torr. – ^{1}H NMR (neat): δ = 0.65.

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