Schmidt, *Acc. Chem. Res.* **1996**, *29*, 451 – 460; S. Braschohs, *thesis*, University of Bonn, **1998**. In catenanes derived from these lactams, however, one amide group of each ring is inverted and the carbonyl points inwards to provide additional hydrogen bonds: S. Ottens-Hildebrandt, M. Nieger, K. Rissanen, J. Rouvinen, S. Meier, G. Harder, F. Vögtle, *J. Chem. Soc. Chem. Commun.* **1995**, 777 – 778; H. Adams, F. J. Carver, C. A. Hunter, *J. Chem. Soc. Chem. Commun.* **1995**, 809 – 810. A rotaxane was reported where one amide bond also seems to be inverted: D. A. Leigh, A. Murphy, J. P. Smart, A. M. Z. Slawin, *Angew. Chem.* **1997**, *109*, 752 – 756; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 752 – 756.

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[6] Rotaxanes are molecular compounds that consist of one or more wheels and penetrating axles that are mechanically bound together and sterically prevented from dethreading by bulky stopper groups at both ends of the axles. Semirotaxanes and pseudorotaxanes are analogous "conventional" inclusion complexes that are not restrained mechanically from dissociation since the axles (here semi- and pseudoaxles, respectively) carry only one stopper or no stopper at all, respectively. We propose semi- and pseudorotaxanes that act as precursors in rotaxane syntheses to be called prerotaxanes. Compare with P. R. Ashton, D. Philp, N. Spencer, J. F. Stoddart, *J. Chem. Soc. Chem. Commun.* **1991**, 1677 – 1679.

[7] The isophthaloylic H-2 proton signals of host **1a** in CD_2Cl_2 shift about 0.7 ppm downfield in the complex with bromide and 0.45 ppm with acetate anions relative to the free host. The complexation-induced shifts of the NH protons are 1.7 and 1.8 ppm, respectively (δ values for the complexes have been extrapolated from the titration curves). Preliminary studies also show that host **1a** can extract Cl^- and Br^- ions in the presence of tetrabutylammonium ions from an aqueous into an organic phase and maintain a clean 1:1 stoichiometry. The phase transfer of oxoanions is currently under investigation; H. Stephan, Forschungszentrum Rossendorf, personal communication.

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[9] Titrations were made by the stepwise addition of a solution of one of the salts to a solution of a macrocycle. Nonlinear curve-fitting of the shift values of all nonoverlapped signals with significant complexation-induced shifts gave the association constants K_a, the average of which is given for each anion. See C. S. Wilcox in *Frontiers in Supramolecular Organic Chemistry and Photochemistry* (Eds.: H.-J. Schneider, H. Dürr), VCH, Weinheim, **1991**, pp. 123 – 143, and references therein.

[10] Addition of triethylammonium 3,5-di-*tert*-butylphenolate to **1a** in CD_2Cl_2 caused only weak chemical shifts. With protonated 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the counterion, the binding constant was about $30\,M^{-1}$. A very tight binding only occured when the phosphazene base "P_4-*t*-Bu" (1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylideneamino]-2λ^5,4λ^5-catenadiphosphazene; Fluka) was used to obtain the phenolate. The "free" anion is probably only formed in the nonpolar environment with this extremely strong, voluminous base. Line-broadening in the presence of less than one equivalent of phenolate **2** makes quantification difficult, but we estimate that at least 95% of the complex is formed at a concentration of 5 mM. The assiociation constant in a mixture of CD_2Cl_2/CD_3OD (4/1) is $280 \pm 10\,M^{-1}$, that is, similar to the inorganic anions. Thiophenol, toluene-4-sulfonamide, and *N*-(4-*tert*-butylphenyl)-4-*tert*-butylphenylsulfonamide behave in a similar way.

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[12] Addition of dibromide **3** or a diphenyl ether derived from it without voluminous stopper groups did not cause any significant NMR shifts of the wheel protons in CD_2Cl_2, hence we assume that the semirotaxanes formed with monoether **4** are not stable and thus do not act as prerotaxanes.

[13] In the syntheses of amide-based rotaxanes we often observed that highly reactive starting compounds such as aliphatic acid chlorides and aliphatic amines tended to produce considerably lower yields of rotaxanes relative to less active aromatic acid chlorides and anilines, respectively. We thus decided not to use preformed phenolate salts here, but rather to create them slowly in situ with a suspension of solid K_2CO_3 as the base.

[14] The rotaxanes show the typical upfield shifts ($\Delta\delta$) of proton signals relative to the free components in the NMR spectra recorded in $CDCl_3$. Selected $\Delta\delta$ values of **5a** (**5b**): Axle: C_2H_4 0.49 (0.46), OCH_2 0.53 (0.48), *p*-xylylene 0.72 (the signal at lower field is overlapped in the free axle here) (0.79 and 0.80), oxophenyl H-2/6 0.37 (0.33); wheel: isophthaloyl H-2 0.46 and 0.48 (0.34 and 0.41).

[15] Deslipping had earlier been observed with similar rotaxanes: M. Händel, M. Plevoets, S. Gestermann, F. Vögtle, *Angew. Chem.* **1997**, *109*, 1248 – 1250; *Angew. Chem. Int. Ed. Engl.* **1996**, *36*, 1199 – 1201. Newer results reveal the process being of first order; F. Vögtle, A. Affeld, C. Heim, unpublished results.

[16] The new method has already been applied successfully to the synthesis of analogous rotaxanes with ester, thioester, sulfide, and acetal axles since the submission of this communication.

Replacement of C–O by P–O in Cyclic Acetals and Ketals**

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Organophosphorus compounds are used in plasticizers, pharmaceuticals, pesticides, and warfare agents. Owing to their wide application, a variety of mass spectrometric techniques have been suggested for their identification[1] and used to study their gas-phase reactivity.[2] Phosphanylium ions (phosphenium ions, $R-P^+-R$), for example, participate in reactions that include insertion, proton transfer, hydride abstraction, electron transfer, cluster formation,[2–4] and [4+2$^+$] cycloaddition.[5] However, most gas-phase ion chemical studies of organophosphorus esters have been limited to characterization of molecular ions and reactions of the ions with their neutral precursors.[1, 4, 6] Methanol, formaldehyde, and alkene eliminations are commonly observed fragmentation processes. The generation and reaction of phosphorus-containing distonic ions has also received attention.[6a, 7]

Aiming to explore the chemistry of phosphoryl-containing cations, and ultimately contribute to increased understanding of the mechanism of hydrolysis of oxyphosphoranes[8] and related phosphoryl-transfer reactions in biomolecules,[9] we report here on the reactions of the phosphonium ions $CH_3P(O)OCH_3^+$ and $CH_3OP(O)OCH_3^+$. Alkyl-substituted 1,3-dioxolanes are chosen as the neutral reactants because of their reactivity with the analogous acylium ions.[10, 11]

In solution, acyl transfer is a well-documented method of converting aldehydes and ketones into acetals and ketals and so protecting or, in the case of transacetalization, transferring the carbonyl group. Eberlin et al. discovered and elucidated

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the mechanism of gas-phase transacetalization involving acylium ions ($RC^+{=}O$) and cyclic acetals and ketals.[10, 11] This reaction occurs by initial O-acylation followed by a ring-opening/ring-reclosing sequence in which a neutral carbonyl compound is eliminated and cyclic "ionic ketals"—in other words, 1,3-dioxo cations and their analogues—are formed. Just as hydrolysis regenerates neutral carbonyl compounds in the condensed phase, so collision-induced dissociation of the resonance-stabilized cyclic 1,3-dioxo cations reforms the acylium ions in high yields in the gas phase.

1,3,2-Dioxaphospholane and related oxyphosphoranes are routinely synthesized by condensation of phosphanes and phosphites with diols or diketones in solution,[12] but net replacement of C–O by P–O in cyclic acetals and ketals through reaction with phosphoryl-containing compounds has not been reported. Mass spectrometry, which offers a unique solvent- and counterion-free environment, is a convenient way to investigate whether cyclic 1,3,2-diheterophospholanium ions can be generated by a transacetalization-like process from phosphoryl-containing ions. These ionic phosphorus-containing derivatives might be useful in protocols for on-line monitoring of phosphorus esters and related warfare agents. Because the polarity of the phosphoryl group is greater than that of the carbonyl group, the cyclic phosphonium ion is much more easily solvated, and ready solvation is the reason that transacetalization reactivity is masked in the condensed phase. Therefore, we explore a general but normally hidden aspect of the reactivity of phosphoryl-containing cations. More importantly, the demonstrated reactivity of the phosphoryl-containing cations provides information that might be useful in searching for deprotecting reagents in less acidic media.

The phosphonium ions $CH_3P(O)OCH_3^+$ (*m*/*z* 93) and $CH_3OP(O)OCH_3^+$ (*m*/*z* 109) were generated from dimethyl methylphosphonate by electron impact (70 eV). All ion–molecule reactions and triple-stage (MS^3) experiments were carried out with a home-built pentaquadrupole mass spectrometer. Ion–molecule reactions of $CH_3P(O)OCH_3^+$ and $CH_3OP(O)OCH_3^+$ with cyclic acetals and ketals occur readily and yield the corresponding 1,3,2-dioxaphospholanium ions. The typical product-ion spectrum for mass-selected $CH_3OP(O)OCH_3^+$ (*m*/*z* 109) reacting with 2-methyl-1,3-dioxolane (*m*/*z* 88) is shown in Figure 1. Proton transfer, methyl cation transfer, and hydride abstraction are major competing reactions.

Scheme 1 outlines a general mechanism for formal replacement of C–O by P–O to yield 1,3,2-dioxaphospholanium ions, and Table 1 lists the collision-induced dissociation (CID)

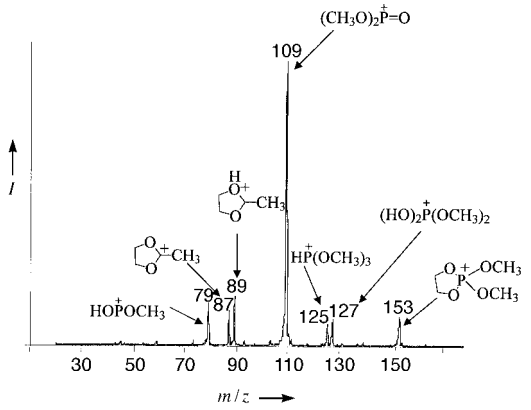
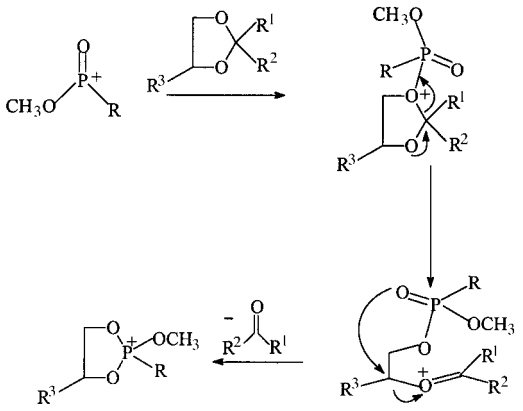


Figure 1. Product ion spectrum for ion–molecule reactions of $CH_3OP(O)OCH_3^+$ (*m*/*z* 109) with 2-methyl-1,3-dioxolane (*m*/*z* 88) at nominally zero kinetic energy. *I* = relative abundance.



Scheme 1. Formal replacement of C–O by P–O to yield 1,3,2-dioxaphospholanium ions. R = OCH_3, CH_3; R^1 = H, CH_3; R^2 = CH_3, C_6H_5; R^3 = H, CH_3.

products of these ions. In most cases, the 1,3,2-dioxaphospholanium ions regenerate the reactant ions in high abundance upon CID. Correspondingly, in solution, 1,3,2-dioxaphospholanes are often hydrolyzed or photolyzed back to the initial phosphonium ions.[12, 13] Direct ketalization of phosphonium ions also occurs in the gas phase, as demonstrated with 2-methoxyethanol and 1,3-propanediol. The resulting product ions arising from loss of CH_3OH or H_2O were shown to have the same structures as those obtained by means of the corresponding transacetalization process.

The reactions displayed by $CH_3P(O)OCH_3^+$ and $CH_3OP(O)OCH_3^+$ can be used to differentiate isomeric acetals and ketals by revealing whether the alkyl substituent is located at

Table 1. Products of transacetalization in ion–molecule reactions with $CH_3P(O)OCH_3^+$ and $CH_3OP(O)OCH_3^+$, and CID fragments of the product 1,3,2-diheterophospholanium ions.

Compound	M_r	Substitution product ion		MS^3 products (*I*)[a]	
		$CH_3P(O)OCH_3^+$	$CH_3OP(O)OCH_3^+$	$CH_3P(O)OCH_3^+$	$CH_3OP(O)OCH_3^+$
2-methyl-1,3-dioxolane	88	137	153	93 (100)	109 (100), 127 (25)
2,2-dimethyl-1,3-dioxolane	102	137	153	93 (100)	109 (100), 127 (25)
4-methyl-1,3-dioxolane	88	151	167	93 (30), 111 (100)	109 (50), 127 (100)
2-phenyl-1,3-dioxolane	150	137	153	93 (100)	109 (100), 127 (30)
thiazolidine	89	136 (20)	152 (20)	–[b]	–[b]
		153 (100)	169 (100)	93 (100), 109 (25)	93 (< 10), 109 (100), 125 (50)

[a] *I* = relative abundance. [b] MS^3 experiments could not be carried out due to the low ion abundance.

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the 2-position. For instance, reaction of $CH_3OP(O)OCH_3^+$ with 2-methyl-1,3-dioxolane gives an intact adduct of *m/z* 153, which dissociates on collision to reform the precursor ion $CH_3OP(O)OCH_3^+$ (*m/z* 109) and protonated dimethyl phosphate $(CH_3O)_2P(OH)_2^+$ (*m/z* 127) through a double hydrogen transfer rearrangement (Figure 2a).[6b, 14] In contrast, $CH_3OP(O)OCH_3^+$ reacts with 4-methyl-1,3-dioxolane to form a product ion 14 Da higher in mass (*m/z* 167), which also dissociates to the initial phosphonium ion and protonated dimethyl phosphate (Figure 2b). These results show that substituents at the 4- and 5-positions remain in the resulting 1,3,2-dioxaphospholanium ions, whereas those at the 2-position are incorporated into the released neutral aldehyde or ketone. Furthermore, the above-mentioned double hydrogen-transfer process is confirmed to involve the ethylene portion of the product 1,3,2-dioxaphospholanium ion.

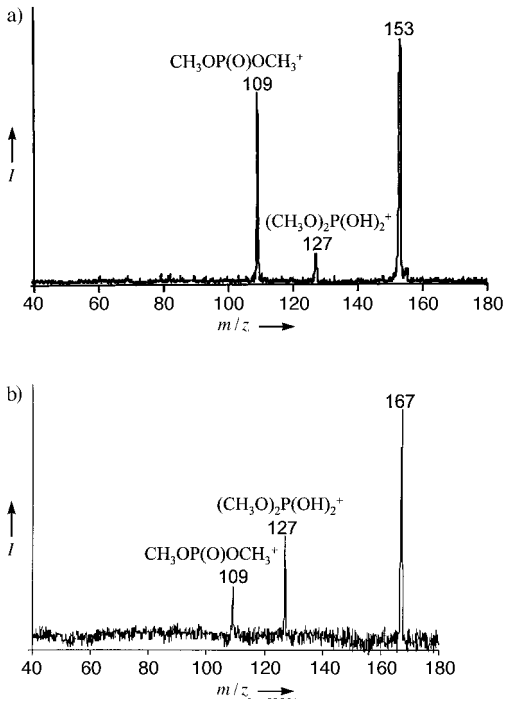
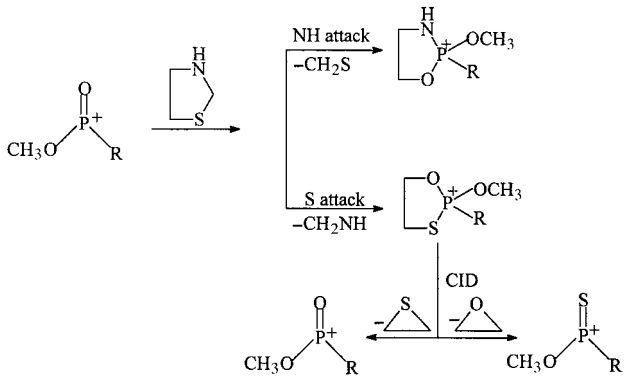


Figure 2. MS^3 sequential product ion spectra for the reaction of $CH_3P(O)OCH_3^+$ (*m/z* 109) with 2-methyl-1,3-dioxolane (a) and 4-methyl-1,3-dioxolane (b). See text for details.

The Eberlin transacetalization is achieved by consecutive electrophilic ring opening and nucleophilic ring closing; hence, reaction rates are sensitive to electronic and steric effects, particularly those due to the 2-substituents.[10, 11] Similar effects are noted in the reactions of $CH_3P(O)OCH_3^+$ and $CH_3OP(O)OCH_3^+$. Reactions with 2-methyl-1,3-dioxolane are faster than those of 4-methyl-1,3-dioxolane, as indicated by the high yield of 1,3,2-dioxaphospholanium ions. This suggests that recyclization induced by the intramolecular nucleophilic attack by the oxygen lone pair is rate limiting.

Thiazolidine has two nucleophilic sites (NH and S); hence it forms two cyclic phospholanium ions in reactions with $CH_3P(O)OCH_3^+$ or $CH_3OP(O)OCH_3^+$. Initial phosphorylation at S yields a 1-oxa-3-thia-2-phospholanium ion, at NH, a 1-aza-3-oxa-2-phospholanium ion. A 5:1 product ratio in favor of reaction at sulfur has been observed for competitive phosphorylation. Furthermore, the 1,3,2-oxathiaphospholanium ions fragment to the initial reactant ions and their thio analogues (Scheme 2) in a ratio of 3:1 for $CH_3P(O)OCH_3^+$ and 2:1 for $CH_3OP(O)OCH_3^+$. This dissociation behavior confirms the cyclic structure of the diheterophospholanium ion, and it also provides a route for conversion of $RRP^+{=}O$ into $RRP^+{=}S$. A corresponding conversion of $RC^+{=}S$ into $RC^+{=}O$ has also been achieved.[15]



Scheme 2. Reaction of $RP(O)OCH_3^+$ with thiazolidine. R = OCH_3, CH_3.

We have found that in the gas phase representative phosphoryl-containing ions undergo structurally diagnostic transacetalization-like reactions with cyclic acetals and ketals to generate 1,3,2-dioxaphospholanium ions with characteristic dissociation behavior. The relatively high efficiency and structural specificity of the replacement of RRC–O by RRP^+–O can be applied potentially to detect organophosphorus esters at trace levels. The methodology utilized here might also provide an alternative route to model phosphoryl migration in biosystems.[9] Furthermore, owing to the importance of carbonyl group deprotection in organic synthesis, which is usually accomplished by aqueous acid hydrolysis, less acidic techniques are needed for acid-sensitive compounds. The use of transition metals and Lewis acids, oxidative methods, and phosphorus- and silicon-based reagents have been developed to meet this need. We describe here the first parallel gas-phase study to explore the nature of the deprotecting phosphorus-based reagents and provide experimental and theoretical thermochemical data on the deprotection process. Finally, the transacetalization reactivity described can be generalized to other ionic Lewis acids and leads to easy access to synthesis and characterization of a variety of transient heterocyclic cations, for example, tricoordinated cyclic boron cations.

Experimental Section

A pentaquadrupole mass spectrometer[16] comprising three mass-analyzing quadrupoles (Q1, Q3, Q5) and two reaction quadrupoles (Q2, Q4) was used for the MS^2 and MS^3 experiments. $CH_3P(O)OCH_3^+$ or $CH_3OP(O)OCH_3^+$ ions were mass-selected by using Q1 and then allowed to undergo ion–molecule reactions with 1,3-dioxolanes or thiazolidine introduced into Q2. The products of the ion–molecule reactions were recorded by scanning Q5 with both Q3 and Q4 set in the broad-band rf-only mode. These products were characterized by MS^3 experiments, in which the 1,3,2-dioxaphospholanium ions formed in Q2 were mass-selected by using Q3 and allowed to

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undergo energetic collisions with argon in Q4, while Q5 was scanned to record the sequential product ion spectrum. Typical reaction energy in Q2 and collision energy in Q4 are 0 eV and 10 eV (under multiple-collision conditions), respectively. All compounds are commercially available and were used without purification.

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Ion-Channel Gating in Transmembrane Receptor Proteins: Functional Activity in Tethered Lipid Membranes**

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In memory of Fritz Jähnig

The opening and closing (gating) of ion channels by ligand binding or by changes in the electrical transmembrane potential is the basis of many cellular signal-transduction processes.[1] Furthermore it is of great pharmaceutical importance that the activity of membrane channels can be modulated by the binding of therapeutic agents and thus the understanding of these molecular interactions is a significant aspect in rational drug discovery and design. An increasing number of membrane channels are found to act as targets for medicines, and since combinatorial libraries of potential therapeutic compounds are growing rapidly, fast and highly sensitive methods for functional drug screening are required.[2] Traditional methods such as patch clamp for the investigation of the function of channel proteins are poorly suited to high throughput screening. As an alternative, tethered lipid membranes[3–6] offer attractive possibilities in this context as indicated by the detection and modulation of the channel activity of the small antibiotic peptide gramicidin.[7]

Here we probe the function of a well-characterized pore-forming, transmembrane receptor protein by the measurement in situ of both the binding of ligands by surface plasmon resonance (SPR) and subsequent changes of the channel activity by impedance spectroscopy (IS).[8, 9]

The receptor protein OmpF was reconstituted into a fluid lipid bilayer coupled to a gold surface through the sulfur groups of so-called thiolipids[4] present in the bilayer at a defined molar ratio (Figure 1). OmpF is a member of the porin family from the outer membrane of *Escherichia coli*. It functions as a trimer folded in the form of transmembrane β-barrels,[10] which form distinct ion channels.[11] This membrane protein is also the receptor for the antibacterial toxin colicin N.[12] The colicins constitute a large family, which all exert their toxicity by initially binding to their receptor by a central region termed the receptor binding R domain.[13] It has been shown recently that, whilst colicin N binds to detergent-solubilized OmpF with a dissociation constant K_d of 1 μM, the

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