[1-(Trimethylsiloxy)alkyl]triphenylphosphonium Salts: Syntheses and Utilization. Comparisons with Analogous Pyridinium Salts

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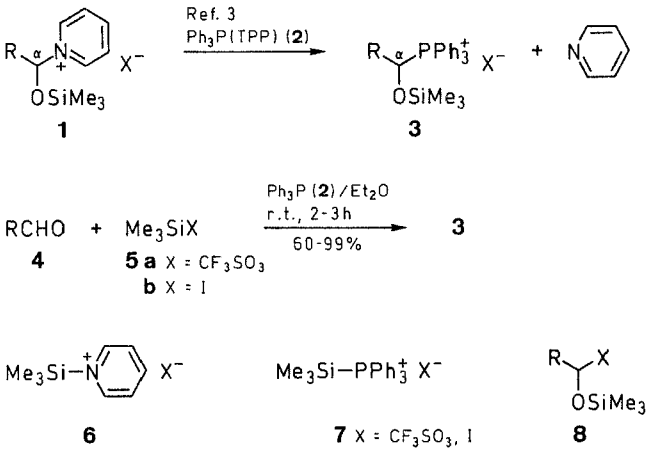
Three-component reactions with aldehydes, trimethylsilyl trifluoromethanesulfonate or iodide, and triphenylphosphine (TPP) yield the title compounds. The X-ray structure of the cationic part of a representative product, the (4-methylphenyl)[(trimethylsiloxy)methyl]TPP$^+$, shows an interesting lengthening of the P$^+$–C(α) bond compared with reported values for methyl(TPP)$^+$ and benzyl(TPP)$^+$ cations (C(α) represents the P-bonded carbon atom of the various alkyl groups). The behavior of the title compounds towards charged nucleophilic reagents and a powerful electrophile (trifluoromethanesulfonic anhydride) is similar to that of analogous pyridinium salts.

In the course of our search for novel group transfer reagents we previously reported the synthesis of 1-[1-(trimethylsiloxy)alkyl]pyridinium salts **1**. The electronic properties of the trimethylsiloxy substituent of **1** result in significant weakening of the N$^+$–C(α) bond, so that the substitution of the pyridinium moiety by a wide variety of uncharged or negatively charged nucleophiles becomes feasible.[3] Reaction with triphenylphosphine (**2**, TPP) transforms the salts **1** into the title compounds, [1-(trimethylsiloxy)alkyl]triphenylphosphonium salts **3**.[3] The successful utilization of salts **1** in syntheses encouraged us to improve access to salts **3** and to investigate their synthetic use. Therefore, we first synthesized a variety of salts **3** and studied their reactivity towards nucleophiles. We then investigated reactions which occur at the trimethylsiloxy group of **3** and compared the results with those using the pyridinium analogs **1** as starting materials.

Though the pyridinium salts **1** may function as precursors of the phosphonium salts **3**, a three-component reaction[4] with aliphatic or aromatic aldehydes **4**, trimethylsilyl triflate or iodide (**5a**[5] or **b**[6]), and TPP **2** proceeds directly to the salts **3** (Scheme 1).

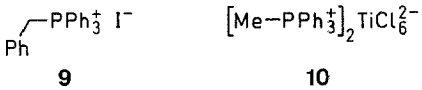
The prior isolation of the *N*-(trimethylsilyl)pyridinium triflate (or iodide) **6** is generally advantageous for the preparation of salts **1**.[3,7] ^{1}H NMR investigations do not indicate any evidence that under the conditions applied a (trimethylsilyl)triphenylphosphonium salt **7**, the analog of **6**, is formed. Furthermore, the sequence in which the three components are added to each other (Scheme 1) does not affect the yields of salts **3**. We assume that the reaction is initiated by the attack of the trimethylsilyl moiety of **5a,b** on the aldehyde oxygen atom, followed by the formation of (non-isolated) intermediates **8**.[8] After reaction with TPP (**2**) compounds **8** are transformed into the title salts. Since the electrophilicity of chlorotrimethylsilane is lower than that of **5a,b**, chlorotrimethylsilane does not undergo a three-component reaction to form chlorides **3**. Yields and data for compounds **3** are summarized in Table 1. These salts are stable for months under nitrogen. After hydrolysis, the aldehydes **4** can be regenerated almost quantitatively.



3, 4	R	X	3, 4	R	X
a	H	CF_3SO_3	**e**	Ph	I
b	Me	I	**f**	4-MeC_6H_4	I
c	Et	CF_3SO_3	**g**	4-MeC_6H_4	CF_3SO_3
d	*i*-Pr	CF_3SO_3			

Scheme 1

The comparison of X-ray structures for (4-methylphenyl)[(trimethylsiloxy)methyl]triphenylphosphonium trifluoromethanesulfonate[9] (**3g**) (Figure) with the related structures **9**[10] and **10**[11] reveals an interesting trend in the P$^+$–C(1) [Scheme 1: P$^+$–C(α)] bond lengths:



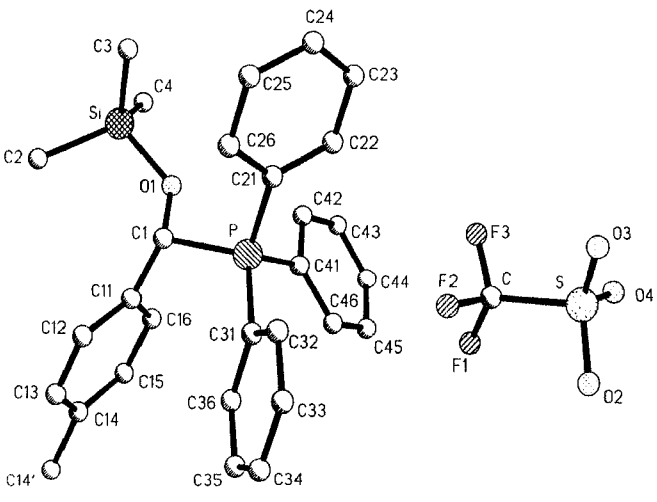


Figure. X-ray analysis of compound **3g** (X-ray analysis numbering).

Table 1. [1-(Trimethylsiloxy)alkyl]triphenylphosphonium Salts **3** Prepared

Product	Yield (%)	mp (°C)	Molecular Formula[a] or Lit. mp (°C)	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)[b]	^{13}C NMR δ, J (Hz)[c]
3a	60	97	$C_{23}H_{26}F_3O_4PSSi$ (514.6)	0.12 (s, 9H), 5.45 (d, 2H, J_{P-H} = 3), 7.60–7.82 (m, 15H)	– 1.18, 58.09 (d, J_{P-C} = 70.19), 116.03 (d, J_{P-C} = 85.45), 130.15 (d, J_{P-C} = 12.97), 133.61 (d, J_{P-C} = 9.92), 135.19 (d, J_{P-C} = 2.29)
3b	80	94	$C_{23}H_{28}IOPSi$ (506.4)	0.12 (s, 9H), 1.73 (dd, 3H, J_{H-H} = 7, J_{P-H} = 18), 6.58 (q, 1H, J = 7), 7.70–8.13 (m, 15H)	–
3c	93	94	$C_{25}H_{30}F_3O_4PSSi$ (542.6)	0.14 (s, 9H), 1.26 (t, 3H, J = 7), 1.78–2.52 (m, 2H) 5.88–6.10 (m, 1H), 7.83–8.20 (m, 15H)	– 0.09, 10.51 (d, J_{P-C} = 12.97), 26.42 (d, J_{P-C} = 4.57), 73.20 (d, J_{P-C} = 62.56), 116.55 (d, J_{P-C} = 80.87), 130.17 (d, J_{P-C} = 12.21), 134.22 (d, J_{P-C} = 8.4), 134.94 (d, J_{P-C} = 2.29)
3d	98	98	$C_{26}H_{32}F_3O_4PSSi$ (556.2)	0.15 (s, 9H), 0.75 (d, 3H, J = 7), 1.05 (d, 3H, J = 7), 2.38 (m, 1H), 5.65 (s, 1H), 7.75 (m, 15H)	–
3e	99	164	$C_{26}H_{30}IOPSi$ (568.5)	0.00 (s, 9H), 7.27–7.88 (m, 21H)	0.00, 72.78 (d, J_{P-C} = 65.61), 115.20 (d, J_{P-C} = 81.63), 127.77, 128.32, 128.53, 129.02, 129.50, 132.63, 134.23, 134.57
3f	97	149	$C_{29}H_{32}IOPSi$ (582.5)	0.03 (s, 9H), 2.33 (d, 3H, J_{P-H} = 3), 6.95–7.78 (m, 21H)	– 0.18, 20.57, 72.49 (d, J_{P-C} = 66.38), 115.14 (d, J_{P-C} = 81.64), 128.26, 128.83, 129.32, 134.02, 134.35, 139.30, 139.42
3g	99	164	162[3]	0.00 (s, 9H), 2.33 (d, 3H, J_{P-H} = 3), 6.78 (d, 1H, J_{P-H} = 4), 7.07–7.87 (m, 15H)	– 0.18, 21.17, 74.12 (d, J_{P-C} = 67.14), 115.84 (d, J_{P-C} = 81.64), 128.59, 128.80, 129.26, 129.53, 129.77, 130.02, 134.53, 134.90, 140.33

[a] Satisfactory microanalysis obtained: C ± 0.31, H ± 0.18. Exception: **2e, f**: C ± 0.47.
[b] Measuring frequency: 60 MHz.
[c] Measuring frequency: 25.1 MHz.

Table 2. X-ray Structures of Some Alkyltriphenylphosphonium Salts: Selected Bond Lengths

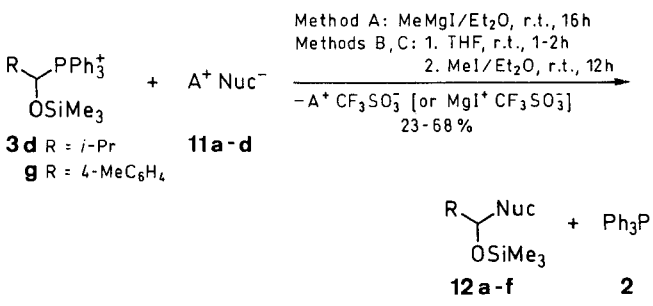
Compound[a]	Bond Lengths (pm) P-C (1)	P-C (21)	P-C (31)	P-C (41)	C (1)-C (11)	C (1)-O (1)	O(1)-Si	Si-(C2)
3a	184.6 (6)	178.2 (5)	179.9 (5)	179.1 (5)	150.7 (7)	139.4 (6)	166.4 (4)	183.7 (7)
9[10]	181.2 (5)	178. (6)	179.6 (6)	179.9 (6)	151.0 (10)	–	–	–
10[11]	178.3 (4)	179.5	–	–	–	–	–	–

[a] For the numbering of atoms: see Figure.

This length increases as the result of the electronic effects of the substituents (methyl-TPP$^+$, **10**: 178.3, benzyl-, **9**: 181.2, 4-(methylphenyl)(trimethylsiloxy)methyl-TPP$^+$, **3a**: 184.6 pm). All the other bond lengths are not affected by these substituents (Table 2). This elongation may parallel the weakening of the P$^+$–C(1) bond strength. In analogy to the properties of salts **1**, the transfer of the alkyl moieties in **3** to nucleophiles might also be feasible. To obtain evidence for this, salts **3** were reacted with a variety of nucleophiles **11a–d** (Scheme 2).

The results can be summarized as follows: Comparable to the reactivity behavior of pyridinium salts **1**, nucleophilic displacement of the phosphonium moiety and formation of products **12a–f** is possible with salts **3**. Nucleophilic displacement reactions of this kind for phosphonium salts are relatively rare.[12]

In both type of salts the trimethylsiloxy substituent is a useful functional group,[13] providing access to a variety of compounds with further synthetic potential. Evidence was obtained by using a powerful electrophilic reagent, trifluoromethanesulfonic anhydride (**13**, TfOTf).[14]



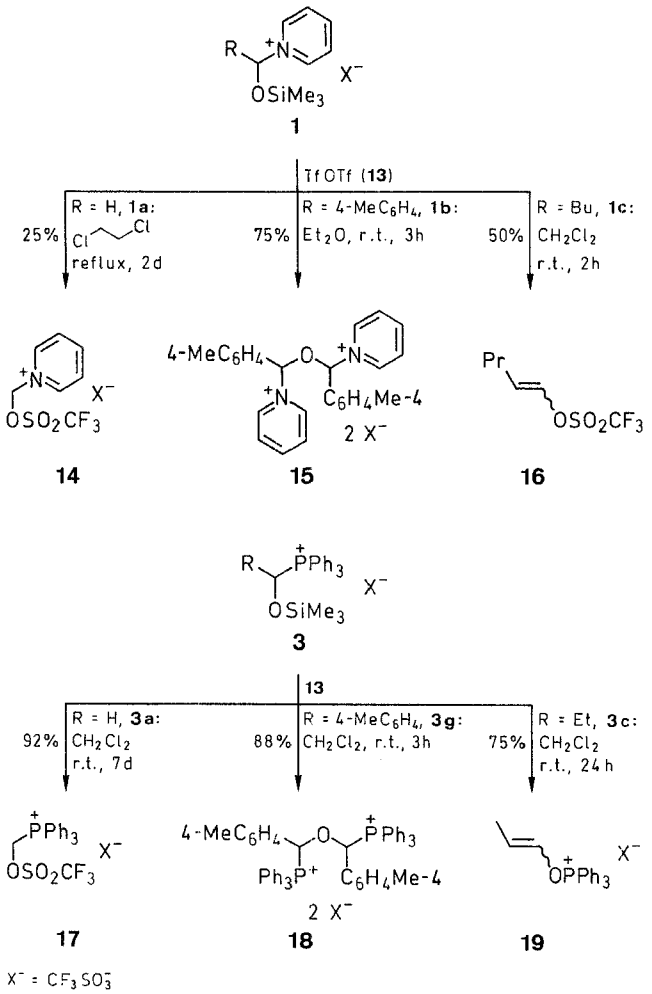
11	A^+Nuc^-	12	R	Nuc	Method; Yield (%) A	B	C	D, Ref. 3
a	K^+Pyrr^-[a]	**a**	*i*-Pr	*Pyrr*	–	*44*	–	–
b	$Et_4N^+CN^-$	**b**	*i*-Pr	CN	–	48	–	46
a	K^+Pyrr^-	**c**	4-MeC_6H_4	Pyrr	–	46	–	22
b	$Et_4N^+CN^-$	**d**	4-MeC_6H_4	CN	–	38	–	68
c	$Na^+CH(CO_2Et)_2$	**e**	4-MeC_6H_4	$CH(CO_2Et)_2$	–	–	23	43
d	MgI-Me	**f**	4-MeC_6H_4	Me	33	–	–	48

[a] Pyrr = pyrrole.

Scheme 2

Table 3. Bond Distances (pm) and Angles (deg) for Compound **3g**

Atoms		Atoms		Atoms		Atoms	
P-C (1)	184.6 (6)	C (24)-C (25)	135.9 (10)	O (1)-Si-C (2)	108.9 (3)	C (32)-C (33)-C (34)	121.5 (6)
P-C (21)	178.2 (5)	C (25)-C (26)	138.8 (9)	O (1)-Si-C (3)	108.8 (3)	C (31)-C (32)-C (33)	118.9 (6)
P-C (31)	179.9 (5)	C (31)-C (32)	137.0 (8)	C (2)-Si-C (3)	111.3 (4)	C (32)-C (31)-C (36)	119.6 (5)
P-C (41)	179.1 (5)	C (31)-C (36)	139.0 (8)	O (1)-Si-C (4)	103.6 (3)	C (33)-C (34)-C (35)	119.3 (6)
C (1)-O (1)	139.4 (6)	C (32)-C (33)	137.7 (9)	C (2)-Si-C (4)	111.7 (4)	C (34)-C (35)-C (36)	120.4 (6)
C (1)-C (11)	150.7 (7)	C (33)-C (34)	137.3 (10)	C (3)-Si-C (4)	112.1 (4)	C (31)-C (36)-C (35)	120.2 (6)
O (1)-Si	166.4 (4)	C (34)-C (35)	135.8 (10)	C (1)-C (11)-C (12)	120.9 (5)	P-C (41)-C (42)	118.8 (4)
Si-C (2)	183.7 (7)	C (35)-C (36)	136.9 (9)	C (1)-C (11)-C (16)	120.2 (5)	P-C (41)-C (46)	121.4 (4)
Si-C (3)	183.4 (7)	C (41)-C (42)	140.3 (8)	C (12)-C (11)-C (16)	118.9 (5)	C (42)-C (41)-C (46)	119.7 (5)
Si-C (4)	180.8 (7)	C (41)-C (46)	138.0 (8)	C (11)-C (12)-C (13)	120.9 (5)	C (41)-C (42)-C (43)	119.3 (5)
C (11)-C (12)	137.2 (8)	C (42)-C (43)	138.7 (9)	C (12)-C (13)-C (14)	120.9 (6)	C (42)-C (43)-C (44)	119.7 (6)
C (11)-C (16)	138.2 (8)	C (43)-C (44)	135.8 (9)	C (13)-C (14)-C (15)	117.9 (6)	C (43)-C (44)-C (45)	121.6 (6)
C (12)-C (13)	136.8 (9)	C (44)-C (45)	136.6 (9)	C (13)-C (14)-C (14')	121.2 (6)	C (44)-C (45)-C (46)	119.9 (6)
C (13)-C (14)	137.8 (9)	C (45)-C (46)	138.2 (9)	C (15)-C (14)-C (14')	120.9 (6)	C (41)-C (46)-C (45)	119.8 (6)
C (14)-C (15)	137.0 (9)	C-F (1)	123.7 (11)	C (14)-C (15)-C (16)	121.9 (6)	F (1)-C-F (2)	105.6 (8)
C (14)-C (14')	151.0 (9)	C-F (2)	136.0 (11)	C (11)-C (16)-C (15)	119.5 (6)	F (1)-C-F (3)	109.1 (8)
C (15)-C (16)	137.8 (8)	C-F (3)	126.6 (11)	P-C (21)-C (22)	121.2 (4)	F (2)-C-F (3)	103.8 (8)
C (21)-C (22)	136.8 (9)	C-S	176.0 (10)	P-C (21)-C (26)	119.5 (4)	F (1)-C-S	118.1 (7)
C (21)-C (26)	138.8 (8)	S-O (3)	138.2 (6)	C (22)-C (21)-C (26)	119.3 (5)	F (2)-C-S	106.9 (6)
C (22)-C (23)	138.1 (9)	S-O (4)	142.7 (9)	C (21)-C (22)-C (23)	120.8 (6)	F (3)-C-S	112.1 (7)
C (23)-C (24)	135.7 (10)	S-O (2)	137.2 (10)	C (22)-C (23)-C (24)	119.7 (7)	C-S-O (3)	107.8 (4)
C (1)-P-C (21)	105.8 (2)	C (31)-P-C (41)	109.1 (2)	C (23)-C (24)-C (25)	120.4 (7)	C-S-O (4)	100.0 (4)
C (1)-P-C (31)	111.5 (3)	P-C (1)-O (1)	104.7 (4)	C (24)-C (25)-C (26)	120.7 (6)	O (3)-S-O (4)	113.5 (4)
C (21)-P-C (31)	109.9 (3)	P-C (1)-C (11)	113.8 (4)	C (21)-C (26)-C (25)	119.0 (6)	C-S-O (2)	103.1 (5)
C (1)-P-C (41)	110.3 (3)	O (1)-C (1)-C (11)	113.0 (4)	P-C (31)-C (32)	119.8 (4)	O (3)-S-O (2)	119.1 (5)
C (21)-P-C (41)	110.2 (3)	C (1)-O (1)-Si	126.7 (3)	P-C (31)-C (36)	120.5 (4)	O (4)-S-O (2)	110.9 (5)



Scheme 3

The structures of the products isolated indicate that the reaction course depends predominantly on the substituent R of the salts **1** and **3** (Scheme 3) and only to a lesser extend on the nature of the "onium" part: Again, both types of salts show similar reactivity trends. The reaction sequences with TfOTf are initiated by the exchange of the trimethylsiloxy by the triflate group. For R = H, the expected intermediates **14** and **17** have been isolated starting from both types of salts. The subsequent transformations depend on the structural properties of these intermediates. All profit from the excellent triflate leaving group ability.[14] Aromatic substituted salts **1** and **3** are transformed to oxygen-bridged bispyridinium[15] or analogous bisphosponium salts[16] (**15** or **18**). Starting with aliphatic groups R in both salts, we isolated the vinyl triflate **16**[17] (from the pyridinium salt **1c**) or the compound type **19** (from the phosphonium salt **3c**).

Compounds **17**, **18**, and the starting salts **3** have potential applications in phosphorous ylid chemistry. The same is true for **14** and **15** in pyridinium salt chemistry.

All reactions were carried out under a purified N_2 atmosphere. Glassware was flame dried and flushed with N_2 before use. All reagents were of commercial quality and freshly distilled or recrystallized. Salt **1b** was prepared according Ref. 7. Hexane, Et_2O and THF were distilled from Na, CH_2Cl_2 and 1,2-dichloroethane from P_2O_5. $CDCl_3$ was stored over molecular sieve. Melting points were taken using a copper block apparatus (Linstrøm) and are uncorrected. Microanalyses were obtained using a Heraeus CHN Mikromar or Heraeus CHN Rapid analyzer. NMR spectra were recorded on an JNM-PMX 60 (JEOL), JNM-PS 100 or JNM-GX 400FT (JEOL) spectrometer (TMS as internal reference).

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($pm^2 \times 10^{-1}$)

	x	y	z	U_{eq} [a]
P	793 (2)	2983 (1)	1166 (1)	44 (1)
C (1)	170 (5)	2051 (3)	1047 (3)	48 (2)
O (1)	− 478 (4)	2035 (2)	315 (2)	53 (1)
Si	− 1877 (2)	1549 (1)	45 (1)	65 (1)
C (2)	− 1762 (8)	668 (4)	516 (4)	104 (3)
C (3)	− 3480 (7)	2028 (5)	317 (5)	110 (4)
C (4)	− 1722 (9)	1479 (5)	− 992 (4)	115 (4)
C (11)	1320 (5)	1498 (3)	1146 (3)	41 (2)
C (12)	1452 (6)	1105 (3)	1814 (3)	53 (2)
C (13)	2527 (6)	621 (4)	1915 (3)	64 (3)
C (14)	3495 (6)	509 (3)	1346 (4)	60 (2)
C (15)	3345 (6)	896 (3)	676 (4)	62 (3)
C (16)	2282 (6)	1392 (3)	569 (3)	55 (2)
C (14')	4693 (6)	− 17 (4)	1458 (4)	93 (3)
C (21)	− 759 (5)	3519 (3)	1215 (3)	46 (2)
C (22)	− 930 (6)	4117 (4)	764 (4)	64 (3)
C (23)	− 2142 (7)	4525 (4)	799 (4)	83 (3)
C (24)	− 3178 (7)	4333 (4)	1286 (4)	76 (3)
C (25)	− 3022 (6)	3747 (4)	1747 (4)	75 (3)
C (26)	− 1818 (6)	3325 (4)	1715 (3)	61 (3)
C (31)	1843 (6)	3089 (3)	2038 (3)	46 (2)
C (32)	1440 (6)	3570 (4)	2589 (3)	58 (2)
C (33)	2278 (7)	3655 (4)	3244 (4)	81 (3)
C (34)	3488 (8)	3262 (4)	3361 (4)	79 (3)
C (35)	3885 (7)	2788 (4)	2811 (4)	63 (3)
C (36)	3069 (6)	2690 (3)	2155 (4)	55 (2)
C (41)	1815 (6)	3246 (3)	355 (3)	44 (2)
C (42)	1195 (6)	3210 (3)	− 389 (3)	53 (2)
C (43)	1987 (6)	3398 (3)	− 1022 (4)	61 (3)
C (44)	3355 (7)	3600 (3)	− 916 (4)	66 (3)
C (45)	3968 (6)	3642 (4)	− 195 (4)	66 (3)
C (46)	3200 (6)	3465 (4)	447 (4)	60 (3)
C	2201 (9)	5564 (5)	1703 (5)	114 (4)
F (1)	3225 (8)	5194 (4)	1521 (5)	226 (4)
F (2)	1703 (8)	5259 (3)	2357 (5)	201 (4)
F (3)	1209 (8)	5473 (4)	1210 (4)	210 (4)
S	2492 (2)	6476 (1)	1910 (1)	92 (1)
O (3)	1221 (6)	6772 (3)	2122 (4)	138 (3)
O (4)	2955 (7)	6717 (4)	1175 (5)	209 (4)
O (2)	3593 (9)	6459 (5)	2439 (6)	230 (5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

[1-(Trimethylsiloxy)alkyl]triphenylphosphonium Salts 3b–g; General Procedure:

To a solution of Ph_3P (**2**; 26.2 g, 100 mmol) and the corresponding aldehyde **4** (100 mmol) in Et_2O (500 mL) the silylating agent **5a,b** (110 mmol) dissolved in Et_2O (50 mL) was added during a period of 2 h. The precipitated products were isolated by suction under N_2, washed well with Et_2O and dried in vacuo (0.01 Torr), (Table 1).

[(Trimethylsiloxy)methyl]triphenylphosphonium Trifluoromethanesulfonate (3a); Typical Procedure:

A round-bottom flask containing paraformaldehyde was heated in an oil bath at 200 °C. In a period of 3 h the resulting formaldehyde gas was passed through a wash bottle filled with glass wool into a solution of Ph_3P (**2**; 28.2 g, 110 mmol) and triflate **5a** (22.2 g, 100 mmol) in Et_2O (500 mL). The mixture was extracted with 5% aq Na_2CO_3 (3 × 100 mL). The organic layer was dried ($MgSO_4$), then the product was precipitated by addition of Et_2O. Salt **3a** was isolated by suction, washed well with Et_2O and dried in vacuo (0.01 Torr), (Table 1).

Regeneration of 4-Methylbenzaldehyde by Hydrolysis of Salt 3g:

H_2O (50 mL) was added to a solution of salt **3g** (5.51 g, 9.1 mmol) in CH_2Cl_2 (25 mL). After stirring for 1 h the organic layer was separated and the aqueous solution was extracted with Et_2O (2 × 20 mL). The combined organic layers were dried ($MgSO_4$), evaporated and the residue was distilled under reduced pressure; yield: 1.01 g (94%).

Substitution Products 12 from Salts 3 with Nucleophiles 11; General Procedures:

Method A: The Grignard reagent obtained from MeI (3.55 g, 25 mmol) and Mg (0.61 g, 25 mmol) in Et_2O (25 mL) was added dropwise to a stirred suspension of salt **3g** in Et_2O (30 mL). After the addition was complete stirring at r.t. is continued for 16 h. The resulting suspension was filtered under N_2. Solvent was evaporated and product **12f** was distilled from the residue using a Kugelrohr apparatus.

1-(4-Methylphenyl)ethyl Trimethylsilyl Ether (**12f**): yield 1.7 g (33%); bp 60–62 °C/0.2 Torr; (Lit.[3] 48%, 60–70 °C/0.2 Torr).

Method B: Salts **3d** or **3g** (10 mmol) were dissolved in THF (50 mL) and the nucleophile **11a** or **11b** was added all at once. The mixture was stirred at r.t. for 1 h. Solvent was removed in vacuo and the residue was suspended in Et_2O (30 mL). The byproducts (A^+X^-, see Scheme 2) were filtered off and an excess of MeI (2.84 g, 20 mmol) was added to the filtrate. After stirring for 12 h the methyltriphenylphosphonium iodide was removed by filtration. After evaporation of the solvent, the products were purified by Kugelrohr distillation. Boiling points and spectroscopic data of **12b–d** correspond to Lit.[3]

1-[2-Methyl-1-(trimethylsiloxy)propyl]pyrrole (**12a**):

From salt **3d** (6.76 g, 12.0 mmol) and nucleophile **11a** (1.28 g, 12.2 mmol) in THF (50 mL), yield: 0.5 g (19%); bp 35–40 °C/0.2 Torr.

$C_{11}H_{21}NOSi$	calc.	C 62.50	H 10.01	N 6.62
(211.38)	found	62.49	9.77	6.45

^1H NMR ($CDCl_3$/TMS): δ = 0.09 [s, 9 H, $Si(CH_3)_3$], 0.69 [d, 3 H, J = 7 Hz, $(CH_3)_2CH$], 1.06 [d, 3 H, J = 7 Hz, $(CH_3)_2CH$], 2.09 [m, 1 H, $(CH_3)_2CH$], 4.94 (d, 1 H, J = 8 Hz, CH), 6.14 (m, 2 H, 3- and 4-H from Pyrr), 6.77 (m, 2 H, 2- and 5-H from Pyrr).

Method C: Salt **3g** was added all at once to a suspension of nucleophile **11c** (10 mmol) in THF (30 mL). The mixture was stirred at r.t. for 2 h. Solvent was evaporated and the residue was suspended in Et_2O (30 mL). The following workup corresponded to Method B. Boiling point and spectroscopic data of **12e** corresponded to Lit.[3]

Reaction Products from [1-(Trimethylsiloxy)alkyl]triphenylphosphonium Salts 3 with Electrophile 13; General Procedure:

After reaction of salts **3** with the electrophile **13** the resulting mixture was concentrated in vacuo to 20 mL. Et_2O was added until complete precipitation of the product, which was isolated by suction, washed well with Et_2O and dried in vacuo (0.01 Torr). When the product did not crystallize immediately by addition of Et_2O, the liquid layer was decanted and the remaining oil was stirred with Et_2O or hexane until crystallization.

[(Trifluormethylsulfonyloxy)methyl]triphenylphosphonium Trifluoromethanesulfonate (**17**):

From salt **3a** (2.9 g, 5.6 mmol) and trifluoromethanesulfonic anhydride (**13**; 3.2 g, 11.3 mmol) in CH_2Cl_2 (40 mL); yield: 3.0 g (92%); mp 72 °C.

$C_{21}H_{17}F_6O_6PS_2$	calc.	C 43.91	H 2.98	
(574.5)	found	43.97	3.04	

IR ($CDCl_3$): ν = 3065 m, 2980 m, 2930 m, 1585 m, 1485 m, 1435 s, 1420 s, 1250 br, 1155 br, 1030 s cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 6.45 (d, 2 H, J_{P-H} = 4 Hz, CH_2), 7.35–8.15 (m, 15 H, H_{arom}).

^{13}C NMR ($CDCl_3$/TMS): δ = 66.28 (d, J_{P-C} = 65.61 Hz, CH_2), 113.59 (d, J_{P-C} = 88.5 Hz, C_{ipso}), 130.91 (d, J_{P-C}) = 12.2 Hz, C_{meta}), 134.15 (d, J_{P-C} = 10.7 Hz, C_{ortho}), 136.45 (C_{para}), 113.38, 116.57, 119.77, 122.96 (q, J_{C-F} = 320.4 Hz, $CF_3SO_3^-$), 115.70, 118.89, 122.08, 125.26 (q, J_{C-F}) = 320.4 Hz, CF_3SO_3C).

Oxybis[(4-methylphenyl)(triphenylphosphonio)methane] Trifluormethanesulfonate **(18)**:

From salt **3g** (4.0 g, 6.6 mmol) and trifluoromethanesulfonic anhydride (**13**; 1.13 g, 4.0 mmol) in CH_2Cl_2 (50 mL); yield: 3.1 g (88%); mp 193°C.

$C_{54}H_{46}F_6O_7P_2S_2$	calc.	C 61.95	H 4.43
(1047.0)	found	61.59	4.45

IR (KBr): ν = 3060 w, 2900 w, 2840 w, 1600 s, 1580 s, 1510 s, 1435 s, 1255 br, 1150 ss, 1025 s cm^{-1}

^1H NMR ($CDCl_3$/TMS): δ = 2.40 (s, 6H, CH_3-Aryl), 6.77–8.00 (m, 40H, CH and H_{arom}).

Triphenyl (1-propenyloxy)phosphonium Trifluoromethanesulfonate **(19)**:

From salt **3c** (4.8 g, 8.9 mmol) and trifluoromethanesulfonic anhydride (**13**; 3.78 g, 13.3 mmol) in CH_2Cl_2 (50 mL); yield: 3.1 g (75%); mp 100°C. A correct microanalysis was not obtained. Impurities were not observed in the NMR spectra.

IR ($CDCl_3$): ν = 3060 w, 1680 w, 1595 m, 1485 w, 1440 s, 1265 br, 1155 br, 1025 s cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 1.69 (m, 3H, *cis/trans* C=CHC$\underline{H}_3$), 1.61 (m, 3H, *cis/trans* C=CHC$\underline{H}_3$), 5.39 (m, 1H, C=C$\underline{H}$CH$_3$), 6.41 (m, 1H, OCH=C), 7.60–7.96 (m, 15H, H_{arom}).

^{13}C NMR ($CDCl_3$): δ = 9.52 (C=CH$\underline{C}$H$_3$), 116.91 (C=$\underline{C}$CH$_3$) 117.0 (O$\underline{C}$H=C), 117.90 (d, J_{P-C} = 105 Hz, P–C_{ipso}), 130.51, (d, J_{P-C} = 13.7 Hz, P–C_{meta}), 133.31 (d, J_{P-C} = 12.2 Hz, P–C_{ortho}), 136.7 (d, J_{P-C} = 2.9 Hz, P–C_{para}).

MS (FD, 2.4 kV, 200°C): m/z = 319 (M^+ of the cation).

1-[(Trimethylsiloxy)methyl]pyridinium Trifluoromethanesulfonate (1a):

From pyridine (7.9 g, 100 mmol), trimethylsilyl triflate **5a** (22.2 g, 100 mmol) and formaldehyde in CH_2Cl_2 (400 mL) analogous to the procedure given for salt **3a**; yield: 33.1 g (70%); mp 25°C.

IR ($CDCl_3$): ν = 2980 m, 2910 w, 1640 m, 1270 br, 1160 br, 1030 s, 855 s cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 0.50 [s, 9H, $Si(CH_3)_3$], 6.35 (s, 2H, CH_2), 8.43 (mc, 2H, 3- and 5-H from Py^+), 8.92 (mc, 1H, 4-H from Py^+), 9.33 (mc, 2H, 2- and 6-H from Py^+).

^{13}C NMR ($CDCl_3$): δ = −0.88 [$Si(CH_3)_3$], 82.42 (CH_2), 128.02 (C_{meta}) from Py^+), 141.64 (C_{ortho}) from Py^+), 146.61 (C_{para} from Py^+).

1-[(1-Trimethylsiloxy)butyl]pyridinium Trifluoromethanesulfonate (1c):

To a solution of the triflate **5a**) (8.5 g), 28 mmol) in CH_2Cl_2 (50 mL) butyraldehyde (2.5 g, 35 mmol) was added. After stirring 15 min at r.t. the mixture was extracted with 5% aq Na_2CO_3 (50 mL). The organic layer was separated, dried ($MgSO_4$) and the product was precipitated by addition of Et_2O. Salt **1c** was isolated by suction, washed well with Et_2O and dried in vacuo (0.01 Torr); yield 3.2 g (30%); mp 202°C.

IR ($CDCl_3$): ν = 3090 w, 2980 s, 1635 s, 1500 s, 1480 s, 1260 br, 1160 br, 1025 s, 845 s cm^{-1}.

^1H NMR ($CDCl_3$/TMS): δ = 0.20 [s, 9H, $Si(CH_3)_3$], 0.77–2.20 (m, 7H, $CH_3CH_2CH_2$), 6.37 (tc, 1H, J_{C-H} = 5.5 Hz, CH), 8.10–9.00 (m, 3H, 3-, 4- and 5-H from Py^+), 9.25 (mc, 2H, 2- and 6-H from Py^+).

^{13}C NMR ($CDCl_3$): δ = −0.88 [$Si(CH_3)_3$], 13.10 ($\underline{C}H_3CH_2CH_2$), 17.17 ($CH_3\underline{C}H_2CH_2$), 41.86 ($CH_3CH_2\underline{C}H_2$), 93.34 (CH), 128.29 (C_{meta} from Py^+), 140.42 (C_{ortho} from Py^+), 146.55 (C_{para} from Py^+).

1-[(Trifluormethylsulfonyloxy)methyl]pyridinium Trifluoromethanesulfonate (14):

Trifluoromethanesulfonic anhydride (**13**; 8.9 g, 40.0 mmol) was added to a solution of salt **1a** (12.7 g, 38.3 mmol) in 1,2-dichloroethane (100 mL). The mixture was heated at reflux for 2 d. The workup was complicated due to the necessity to separate the salt **14** from a salt-like by-product, presumably methylenebispyridinium triflate. Both compounds formed an oil from which minor amounts of **14** could be extracted. The major amount of **14** remained dissolved in 1,2-dichloroethane, from which it crystallized at −18°C. Details: After cooling to r.t. the mixture was decanted from the insoluble oil (see above). EtOAc (100 mL) was added to the solution to precipitate further bispyridinium salt. After filtration the solvents were evaporated and the residue was dissolved by heating in 1,2-dichloroethane (100 mL). Standing overnight at −18°C, product **14** crystallized; 3.7 g (25%); mp 55°C.

$C_8H_7NF_6O_6S_2$	calc.	C 24.56	H 1.80	N 3.58
(391.3)	found	24.48	1.91	3.54

IR (CD_3CN): ν = 3080 s, 1635 s, 1490 s, 1425 s, 1250 br, 1150 br, 1025 s cm^{-1}.

^1H NMR (CD_3CN/TMS): δ = 7.02 (s, 2H, CH_2), 8.35–9.33 (m, 5H, H_{arom}).

^{13}C NMR (CD_3CN): δ = 87.34 (CH_2), 130.30 (C_{meta} from Py^+), 146.51 (C_{ortho} from Py^+), 151.44 (C_{para} from Py^+), 114.45, 117.62, 120.80, 123.98 (q, J_{C-F} = 318.9 Hz), $CF_3SO_3^-$ 117.11, 120.30, 123.48, 126.67 (q, J_{C-F} = 320.4 Hz, $\underline{C}F_3SO_3C$).

Oxybis[(4-methylphenyl)(1-pyridino)methane] Bis(trifluoromethanesulfonate) (15):

Trifluoromethanesulfonic anhydride (**13**; 1.13 g, 4 mmol) was added to a solution of salt **1b** (3.0 g, 7 mmol) in CH_2Cl_2 (50 mL). After stirring at r.t. for 3 h, the product was precipitated by addition of Et_2O. For further purification the salt was dissolved in CH_2Cl_2, stirred with Na_2CO_3 for 1 h. After filtration the solvent was removed until the solution started to become turbid. For complete crystallization this solution was allowed to stand overnight at −18°C; yield: 3.6 g (75%); mp 166°C.

$C_{28}H_{26}F_6N_2O_7S_2$	calc.	C 49.41	H 3.85	N 4.12
(680.6)	found	49.33	3.88	4.31

IR ($CDCl_3$): ν = 3070 m, 1645 m, 1515 m, 1500 m, 1265 ss, 1170 ss, 1040 s cm^{-1}.

^1H NMR (DMSO/$CDCl_3$/TMS): δ = 2.34 (s, 6H, CH_3-Aryl), 7.17–7.68 (m, 8H, H_{arom}) 7.77 (s, 2H, CH), 7.93–8.06 (mc, 4H, 3- and 5-H from Py^+), 8.58 (mc, 2H, 4-H from Py^+), 9.28 (mc, 4H, 2- and 6-H from Py^+).

^{13}C NMR (DMSO/$CDCl_3$/TMS): δ = 20.59 (CH_3), 126.03, 128.15, 128.23, 132.74, 140.67, 143.84, 145.00 (C_{arom}).

1-Pentenyl Trifluoromethanesulfonate (16):

Trifluoromethanesulfonic anhydride (**13**; 4.6 g, 16.4 mmol) was added to a solution of salt **1c** (5.3 g, 13.7 mmol) in CH_2Cl_2 (50 mL). After stirring at r.t. for 2 h the solvent was removed and the residue was distilled in a Kugelrohr apparatus. The distillate was extracted with H_2O/CH_2Cl_2, dried ($MgSO_4$) and distilled again; yield: 1.5 g (50%); bp 40–45°C/17 Torr; (Lit.[17] 40%, bp 71–73°C/48 Torr).

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