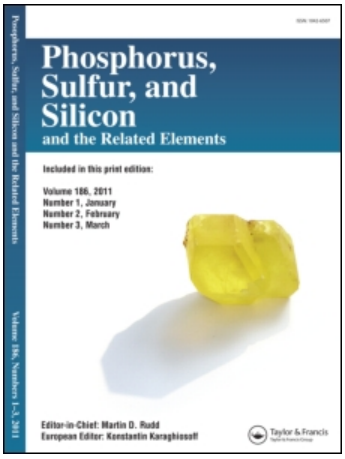

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A Convenient Synthesis Of Phosphorus And Sulfonyl Substituted *N*-Imidazoles (Triazoles) Using The Corresponding Acid Chlorides And *N*-Trimethylsilyl Imidazoles (Triazoles)

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A CONVENIENT SYNTHESIS OF PHOSPHORUS AND SULFONYL-SUBSTITUTED *N*-IMIDAZOLES (TRIAZOLES) USING THE CORRESPONDING ACID CHLORIDES AND *N*-TRIMETHYLSILYL IMIDAZOLES (TRIAZOLES)

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The synthetic route phosphorus and sulfonyl-substituted *N*-imidazoles (triazoles) has been elaborated based on the method proposed by Birkofer[8] *et al.* The appropriate compounds are obtained in high yield and of analytical purity by the action of *N*-trimethylsilyl imidazole (triazole) on the corresponding acid chlorides.

In recent papers[1-3] from this laboratory we have described methods for the synthesis of mixed anhydrides of phosphorus and sulfonic acids based on phosphorus acids and sulfonic acids imidazolides (triazolides) as starting materials.

Phosphorus and sulfonic acids imidazolides (triazolides) are widely used as phosphorylating[4] and sulfonylating[5] reagents. The imidazolides (triazolides) under discussion are usually produced by reaction of the corresponding acid chlorides with two moles of heterocyclic base or in the presence of tertiary amines.[5,6]

$$\rangle P(O)Cl + 2HN\triangleleft \rightarrow \rangle P(O)N\triangleleft + \triangleright NH \cdot HCl$$

$$-SO_2Cl + 2HN\triangleleft \rightarrow -SO_2N\triangleleft + \triangleright NH \cdot HCl$$

$$\rangle NH = \text{Imidazol or 1,2,4-Triazol}$$

In special cases the imidazolides can be prepared from pyrophosphates.[7]

$$\rangle P(O)-O-P(O)\langle + 2HN\triangleleft \quad \rangle P(O)N\triangleleft + \rangle P(O)OH \cdot HN\triangleleft$$

In the procedures mentioned above isolation of pure imidazolides (triazolides) is difficult or impracticable. The need for easily available pure imidazolides (triazolides) turned our attention to the reaction between *N*-trimethylsilylimidazole (triazole) and the acid chlorides which is analogous to that applied by Birkofer *et al.*[8] for the preparation of phosphorus and phosphoric triimidazolides. The reaction of *N*-trimethylsilylimidazole (triazole) **10** with the corresponding acid chlorides pro-

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TABLE I

Preparation of imidazolides

Substrate	Product	Yield (%)	b.p./torr or m.p.[a] (°C)	Molecular formula[b] or lit. b.p./torr or m.p. (°C)	^{31}P-NMR δ (ppm)[c]	^{1}H-NMR ($CDCl_3$/TMS) δ (ppm)[d]
1, R = Me	**2**	91[e]	90–92 (benzene)	$C_4H_6N_2O_2S$ (146.2)	—	3.5 (s, 3 H); 7.3 (s, 1 H) 7.6 (s, 1 H); 8.2 (s, 1 H)
1, R = p-$CH_3C_6H_4$	**2**	100[f]	77–79	78–79[5]		
2,4,6-Triisopropyl benzenesulfonyl chloride	**2**	100[f]	122–124	116–117[5]		
3, R^1 = R^2 = EtO	**4**	100[f]	oil	$C_7H_{13}N_2O_3P$ (204.2)	−6.4 (neat)	1.3–1.9 (t, 6 H, CH_3); 4.2–4.9 (m, 4 H, OCH_2); imidazole ring 7.3 (s, 1 H); 7.6 (s, 1 H); 8.2 (s, 1 H)
3, R^1 = R^2 = i-PrO	**4**	100[f] 91[i]	oil 75/0.15	$C_9H_{15}N_2O_3P$ (232.2)	−8.3 (neat)	1.5 (d, 12 H, CH $(CH_3)_2$, J_{HH} = 6 Hz); 4.5–5.2 m, 2 H, $CHMe_2$; imidazole ring 7.3 (s, 1 H); 7.6 (s, 1 H); 7.6 (s, 1 H); 8.2 (s, 1 H)
3, R^1 = *t*-Bu; R^2 = MeO	**4**	89[e]	125–127 (THF)	$C_8H_{15}N_2O_2P$ (202.2)	35.281 ($CDCl_3$)	1.2 (d, 9 H, J_{PCCH} = 16 Hz); 4.0 (d, 3 H, J_{POCH} = 13 Hz) imidazole ring 7.4 (s, 1 H); 8.2 (s, 1 H); 8.4 (s, 1 H)
3, R^1 = R^2 = Ph	**4**	100[f]	solid	$C_{15}H_{13}N_2OP$ (268.3)	+23.4 ($CDCl_3$)	imidazole ring 7.4 (s, 1 H); 7.7 (s, 1 H); 8.4 (s, 1 H); 7.8–8.1 (m, 10 H_{arom})

5, $R^1 = R^2 =$ EtO	**6**	100[f]	oil	$C_7H_{13}N_2O_2PS$ (220.2)	+58.4 (neat)	
7, $R^1 = R^2 =$ EtO	**8**	100[f]	oil	$C_7H_{13}N_2O_2P$	+135.6 (neat)	1.2–1.4 (m, 6 H); 3.7–4.2 (m, 4 H); 7.2 (s, 2 H); 7.9 (s, 1 H)
7, $R^1 =$ *t*-Bu; R = Ph	**8**	90[i,j]	40/0.01	$C_{13}H_{17}N_2P$ (232.3)	+67.2 (neat)	1.4 (d, 9 H, J_{PHCH} = 18 Hz); 7.6–7.9 (m, 5 H_{arom}); imidazole ring 7.4 (s, 2 H); 8.2 (s, 1 H)
7, $R^1 = R^2 =$ Ph	**8**	100[f,h]	solid	$C_{15}H_{13}N_2P$ (252.3)	+45.4 ($CDCl_3$)	7.6–7.8 (m, 10 H_{arom}); imidazole ring 7.5 (s, 2 H); 8 (s, 1 H)
1, R = Me_3SiO	**2**	90[f]	solid	$C_6H_{12}N_2O_3SSi$ (221.1)	—	1.3 (s, 9 H) imidazole ring 8.2 (s, 1 H); 9.1 (s, 1 H); 9.5 (s, 1 H)
$PhP(O)Cl_2$	$PhP(O)[N\triangleleft N]_2$ **12**	89[e] 100[f]	106–108 (benzene)	$C_{12}H_{11}N_4OP$ (258.3)	+7.2 ($CDCl_3$)	7.8 – 8.1 (m, 10 H_{arom}); imidazole ring 7.2 (s, 2 H); 7.7 (s, 2 H); 8.2 (s, 2 H)
t-$BuPCl_2$	*t*-$BuP[N\triangleleft N]_2$ **13**	100[f] 90[i,j]	120/0.01	$C_{10}H_{15}N_2P$ (202.2)	+82.3 ($CDCl_3$)	1.2 (d, 9 H, J_{PHCH} = 17 Hz); imidazole ring 7.4 (s, 2 H); 7.8(s, 2 H); 8.2 (s, 2 H)

[a] The melting points are uncorrected.
[b] The microanalyses were in good agreement with the calculated values: [c] C ± 0.2%; H ± 0.1%; N ± 0.1%; S ± 0.2%; P ± 0.1%.
[c] Measured with a Jeol INM-FX 60 spectrometer, H_3PO_4 (96%) as standard.
[d] ^{1}H-NMR spectra were recorded at 60 Hz using a Perkin-Elmer R-12 instrument.
[e] Yield of recrystallized product. The yield is calculated on the acid chloride. High purity of products was confirmed by ^{1}H-NMR and ^{31}P-NMR spectroscopy and microanalyses.
[g] Decomposes on attempted distillation.
[h] Decomposes on storning.
[i] Yield of distilled product.
[j] Isolated as oil which solidified after distillation.

ceeds smoothly in dichloromethane at 0°C.

$$\underset{\mathbf{1}}{RSO_2Cl} + \underset{\mathbf{10}}{Me_3SiN\triangleleft} \rightarrow \underset{\mathbf{2}}{RSO_2N\triangleleft} + Me_3SiCl$$

$$\underset{\mathbf{3}}{R^1R^2P(O)Cl} + \underset{\mathbf{10}}{Me_3SiN\triangleleft} \rightarrow \underset{\mathbf{4}}{R^1R^2P(O)N\triangleleft} + Me_3SiCl$$

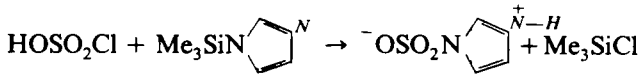
$$\underset{\mathbf{5}}{R^1R^2P(S)Cl} + \underset{\mathbf{10}}{Me_3SiN\triangleleft} \rightarrow \underset{\mathbf{6}}{R^1R^2P(S)N\triangleleft} + Me_3SiCl$$

$$\underset{\mathbf{7}}{R^1R^2PCl} + \underset{\mathbf{10}}{Me_3SiN\triangleleft} \rightarrow \underset{\mathbf{8}}{R^1R^2PN\triangleleft} + Me_3SiCl$$

In most cases, products can be prepared in quantitative yield by evaporation of the solvent and trimethylsilylchloride and are of analytical purity. An additional advantage of the method lies in its simplicity and commercial availability of trimethylsilylimidazole. It is also note-worthy to point out that the method can be employed for the preparation of derivatives which are hardly available by other methods, e.g. imidazolides and triazolides of thio- or selenophosphorus acid. Compounds **6** and **9**[9] can be readily obtained by addition of elemental sulfur or selenium to the tricordinate imidazolide or triazolide **8**.

$$\underset{\mathbf{8}}{R^1R^2PN\triangleleft} \xrightarrow{Se} \underset{\mathbf{9}}{R^1R^2P(Se)N}$$
$$\underset{\mathbf{8}}{R^1R^2PN\triangleleft} \xrightarrow{S} \underset{\mathbf{6}}{R^1R^2P(S)N\triangleleft}$$

The method can be also employed for the preparation of di-*N*-imidazolides of tri- and tetracoordinate phosphorus acids see Table I, compounds **12** and **13**. The applicability of the method can be further illustrated by the reaction between chlorosulfonic acid and *N*-trimethylsilylimidazole leading to the compound **11**.[12]



10 **11**

The structure of **11** confirmed by microanalysis and ^{1}H-NMR spectrum is analogous with that of Pyridine–SO_3 complex.[10]

GENERAL PROCEDURE

A solution of **10** (0.1 mol) in 20 ml of dry dichloromethane was added into the stirred solution of corresponding acid chlorides (0.11 mol) in 10 ml of dry dichloromethane at 0°C. The reaction mixture was stirred for 1 h at room temperature. The solvent, chlorotrimethylsilane formed and excess of *N*-trimethylsilylimidazole (triazole) were removed under reduced pressure of 15 mmHg at 25°C yielding pure imidazolides or triazolides, respectively.

Analogous procedure can be used for the preparation of the di-*N*-imidazolides **12**, **13**. The compound **11** was prepared according to the general procedure.

TABLE II

Preparation of 1,2,4-triazolides

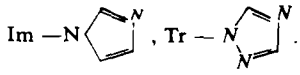
Substrate	Product	Yield	b.p./torr or m.p.[a] (°C)	Molecular formula[b] or Lit. b.p./torr or m.p. (°C)	^{31}P-NMR δ (ppm)[c]	^{1}H-NMR ($CDCl_3$/TMS) δ (ppm)[d]
1, R = Me	**2**	100[e]	96–98	$C_3H_5N_3O_2S$ (147.2)	- -	3.9 (s, 3 H); triazole ring 8.5(s, 1 H); 9.2(s, 1 H).
1, R = p-$CH_3C_6H_4$	**2**	100[e]	107–109	107[4]	—	
2,4,6-Tri-isopropyl benzenesulfonyl chloride	**2**	100[e]	110	112[4]	—	
3, $R^1 = R^2$ = RtO	**4**	100[e] 70[f]	60/0.15	$C_6H_{12}N_3O_3P$ (206.0)	−9.9 (NEAT)	1.6–1.9 (t, 6 H); 4.4–4.9 (M, 4 H) triazole ring 8.6 (s, 1 H); 9.1 (s, 1 H)
5, $R^1 = R^2$ = EtO	**6**	100[e]	oil	$C_6H_{12}N_3O_2PS$ (222.0)	+54.7 (neat)	1.3–1.6 (t, 6 H); 4.2–4.8 (m, 4 H) triazole ring 8.4 (s, 1 H); 9 (s, 1 H)
7, $R^1 = R^2$ = EtO	**8**	100[e] 40[f]	oil 80/0.01	$C_6H_{12}N_3O_2P$ (190.0)	+123.6 (neat)	1.4–1.8 (t, 6 H); 3.9–4.5 (m, 4 H) triazole ring 8.6 (s, 2 H)

[a] The melting points are uncorrected.
[b] The microanalyses were in good agreement with the calculated values C ±0.2%, H ±0.2%; N ±0.1%; S ±0.1%.
[c] Measured with a Jeol INM-EX 60 Spectrometer, H_3PO_4 (96%) as standard.
[d] ^{1}H-NMR specra were recorded at 60Hz using Perkin-Elmer R-12 instrument.
[e] The yield is calculated on the acid chloride. High purity of products was confirmed by ^{1}H-NMR and ^{31}P-NMR spectroscopy and microanalyses.
[f] Yield of distilled products.

TABLE III

Microanalyses *N*-imidazolides triazolides

Product	Molecular Formula	Calculated					Found				
		C	H	N	P	S	C	H	N	P	S
CH_3SO_2Im	$C_4H_6N_2O_2S$ (146.2)	32.9	4.1	19.2	—	21.9	33.1	4.0	19.4	—	21.8
$(C_2H_5O)_2P(O)Im$	$C_7H_{13}N_2O_3P$ (204.2)	41.2	6.4	13.7	15.2	—	41.0	6.4	13.9	15.2	—
$(C_3H_7O)_2P(O)Im$	$C_9H_{15}N_2O_3P$ (232.2)	46.6	6.5	12.1	13.3	—	46.6	6.3	12.0	13.1	—
t-Bu(MeO)P(O)Im	$C_8H_{15}N_2O_2P$ (202.2)	47.5	7.5	13.9	15.3	—	47.2	7.4	13.9	15.2	—
$(C_2H_5O)_2P(S)Im$	$C_7H_{13}N_2O_2PS$ (220.2)	38.2	6.0	12.7	14.1	14.1	38.1	6.0	12.7	14.2	14.7
t-Bu(Ph)PIm	$C_{13}H_{17}N_2P$ (232.3)	67.2	7.4	12.1	13.3	—	67.2	7.0	12.0	13.2	—
$(C_6H_5)_2PIm$	$C_{15}H_{13}N_2P$ (252.3)	71.4	5.2	11.1	12.3	—	71.2	5.0	11.0	12.2	—
Me_3SiOSO_2Im	$C_6H_{12}N_2O_3SSi$ (221.1)	32.6	5.8	12.7	—	14.5	32.4	5.8	12.5	—	14.3
$C_6H_5P(O)Im_2$	$C_{12}H_{11}N_4OP$ (258.3)	55.8	4.3	21.7	12.0	—	55.7	4.2	21.8	12.1	—
t-BuPIm$_2$	$C_{10}H_{15}N_4P$ (222.2)	54.1	6.8	25.2	14.0	—	54.0	6.8	25.2	14.1	—
CH_3SO_2Tr	$C_3H_5N_3O_2S$ (147.2)	24.5	3.4	28.5	—	21.7	24.6	3.6	28.6	—	21.7
$(C_2H_5O)_2P(O)Tr$	$C_6H_{12}N_3O_3P$ (206.0)	35.0	5.8	20.4	15.1	—	35.1	5.9	20.5	15.1	—
$(C_2H_5O)_2P(S)Tr$	$C_6H_{12}N_3O_2PS$ (220.0)	32.7	5.5	19.1	14.1	14.6	32.7	5.4	19.0	14.1	14.5
$(C_2H_5O)_2PTr$	$C_6H_{12}N_3O_2P$ (190.0)	37.9	6.3	22.1	16.3	—	37.9	6.2	22.0	16.2	—



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12. ^{1}H-NMR ($CDCl_3$) imidazole ring 7.9 (s, 1 H); 9.1 (s, 1 H); 9.3 (s, 1 H); 13.4 (s, 1 H) $C_3H_4N_2O_3S$ (148.1): Calc.: C, 24.3; H, 2.7; N, 18.9, S, 21.6%. Found: C, 24.4; H, 2.9; N, 19.1; S, 21.4%. t.t. 112–116 (CH_3COCH_3/CH_2Cl_2). Yield of recrystallized product 91%.
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