

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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

W. Dąbkowski^a; J. Michalski^a; Z. Skrzypczyński^a

^a Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Boczna 5, Lodz, Poland

To cite this Article Dąbkowski, W. , Michalski, J. and Skrzypczyński, Z.(1986) 'A Convenient Synthesis Of Phosphorus And Sulfonyl Substituted *N*-Imidazoles (Triazoles) Using The Corresponding Acid Chlorides And *N*-Trimethylsilyl Imidazoles (Triazoles)', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 26: 3, 321 — 326

To link to this Article: DOI: 10.1080/03086648608084586

URL: <http://dx.doi.org/10.1080/03086648608084586>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

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

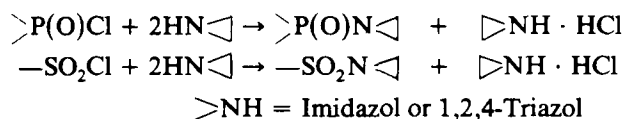
W. DĄBKOWSKI, J. MICHALSKI* and Z. SKRZYPCZYŃSKI

*Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies,
Boczna 5, 90-362 Łódź, Poland*

The synthetic route phosphorus and sulfonyl-substituted *N*-imidazoles (triazoles) has been elaborated based on the method proposed by Birkofer⁸ *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 papers¹⁻³ 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 phosphorylating⁴ and sulfonylating⁵ 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}



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



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-

*Author to whom all correspondence should be addressed.

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 ₄ H ₆ N ₂ O ₂ S (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 ₃ C ₆ H ₄	2	100 ^f	77–79	78–79 ⁵		
2, 4, 6-Trisopropyl benzenesulfonyl chloride	2	100 ^f	122–124	116–117 ⁵		
3, R ¹ = R ² = EtO	4	100 ^f	oil	C ₇ H ₁₃ N ₂ O ₃ P (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 ₉ H ₁₅ N ₂ O ₃ P (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 = <i>t</i> -Bu; R ² = MeO	4	89 ^e	125–127 (THF)	C ₈ H ₁₅ N ₂ O ₂ P (202.2)	35.281 (CDCl ₃)	1.2 (d, 9 H, J _{POCH} = 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 ₂ OP (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 7, R ¹ = R ² = EtO	6 8	100 ^f 100 ^f	oil oil	C ₇ H ₁₃ N ₂ O ₂ PS (220.2) C ₇ H ₁₃ N ₂ O ₂ P	+ 58.4 (neat) + 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 = <i>i</i> -Bu; R = Ph	8	90 ^{h,j}	40/0.01	C ₁₃ H ₁₇ N ₂ P (232.3)	+ 67.2 (neat)	1.4 (d, 9 H, <i>J</i> _{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 ^h	solid	C ₁₃ H ₁₃ N ₂ P (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 ₃ SiO	2	90 ^f	solid	C ₆ H ₁₂ N ₂ O ₃ SSI (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<N] ₁₂	89 ^e 100 ^f	106–108 (benzene)	C ₁₂ H ₁₁ N ₄ OP (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)
<i>i</i> -BuPCL ₂	<i>i</i> -BuP[N<N] ₁₃	100 ^f 90 ^{h,j}	120/0.01	C ₁₀ H ₁₅ N ₂ P (202.2)	+ 82.3 (CDCl ₃)	1.2 (d, 9 H, <i>J</i> _{PHCH} = 17 Hz); imidazole ring 7.4 (s, 2 H); 7.8 (s, 2 H)

^aThe melting points are uncorrected.

^bThe microanalyses were in good agreement with the calculated values: ^cC ± 0.2%; H ± 0.1%; N ± 0.1%; S ± 0.2%; P ± 0.1%.

^cMeasured with a Jeol INM-FX 60 spectrometer, H₃PO₄ (96%) as standard.

^d¹H-NMR spectra were recorded at 60 Hz using a Perkin-Elmer R-12 instrument.

^eYield of recrystallized product. The yield is calculated on the acid chloride. High purity of products was confirmed by ¹H-NMR and ³¹P-NMR spectroscopy and microanalyses.

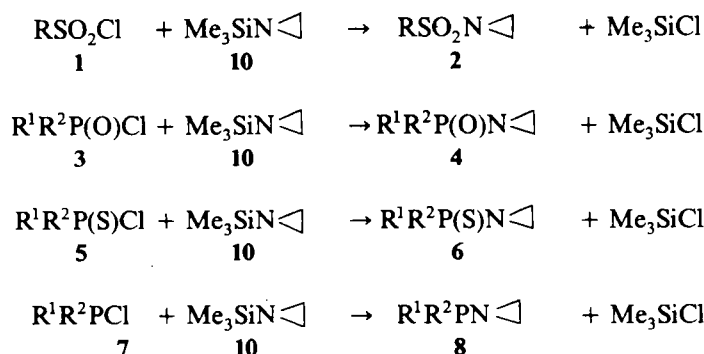
^gDecomposes on attempted distillation.

^hDecomposes on storing.

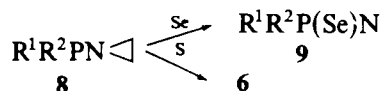
ⁱYield of distilled product.

^jIsolated as oil which solidified after distillation.

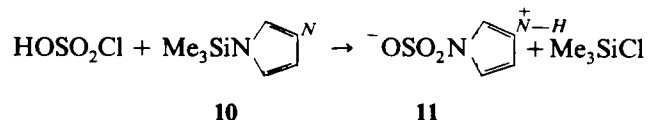
ceeds smoothly in dichloromethane at 0°C.



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** can be readily obtained by addition of elemental sulfur or selenium to the tricordinate imidazolidine or triazolide **8**.



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



The structure of **11** confirmed by microanalysis and ¹H-NMR spectrum is analogous with that of Pyridine-SO₃ 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.

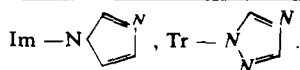
Analogous procedure can be used for the preparation of the di-*N*-imidazolides **12**, **13**. The compound **11** was prepared according to the general procedure.

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 ₃ H ₃ N ₃ O ₂ S (147.2)	—	3.9 (s, 3 H); triazole ring 8.5 (s, 1 H); 9.2 (s, 1 H).
1, R = p-CH ₃ C ₆ H ₄	2	100 ^e	107-109	107 ^d	—	
2,4,6-Tri-isopropyl benzenesulfonyl chloride	2	100 ^e	110	112 ^d	—	
3, R ¹ = R ² = R ³ = R ⁴ = R ⁵ = R ⁶ = R ⁷ = R ⁸ = R ⁹ = R ¹⁰ = R ¹¹ = R ¹² = R ¹³ = R ¹⁴ = R ¹⁵ = R ¹⁶ = R ¹⁷ = R ¹⁸ = R ¹⁹ = R ²⁰ = R ²¹ = R ²² = R ²³ = R ²⁴ = R ²⁵ = R ²⁶ = R ²⁷ = R ²⁸ = R ²⁹ = R ³⁰ = R ³¹ = R ³² = R ³³ = R ³⁴ = R ³⁵ = R ³⁶ = R ³⁷ = R ³⁸ = R ³⁹ = R ⁴⁰ = R ⁴¹ = R ⁴² = R ⁴³ = R ⁴⁴ = R ⁴⁵ = R ⁴⁶ = R ⁴⁷ = R ⁴⁸ = R ⁴⁹ = R ⁵⁰ = R ⁵¹ = R ⁵² = R ⁵³ = R ⁵⁴ = R ⁵⁵ = R ⁵⁶ = R ⁵⁷ = R ⁵⁸ = R ⁵⁹ = R ⁶⁰ = R ⁶¹ = R ⁶² = R ⁶³ = R ⁶⁴ = R ⁶⁵ = R ⁶⁶ = R ⁶⁷ = R ⁶⁸ = R ⁶⁹ = R ⁷⁰ = R ⁷¹ = R ⁷² = R ⁷³ = R ⁷⁴ = R ⁷⁵ = R ⁷⁶ = R ⁷⁷ = R ⁷⁸ = R ⁷⁹ = R ⁸⁰ = R ⁸¹ = R ⁸² = R ⁸³ = R ⁸⁴ = R ⁸⁵ = R ⁸⁶ = R ⁸⁷ = R ⁸⁸ = R ⁸⁹ = R ⁹⁰ = R ⁹¹ = R ⁹² = R ⁹³ = R ⁹⁴ = R ⁹⁵ = R ⁹⁶ = R ⁹⁷ = R ⁹⁸ = R ⁹⁹ = R ¹⁰⁰ = R ¹⁰¹ = R ¹⁰² = R ¹⁰³ = R ¹⁰⁴ = R ¹⁰⁵ = R ¹⁰⁶ = R ¹⁰⁷ = R ¹⁰⁸ = R ¹⁰⁹ = R ¹¹⁰ = R ¹¹¹ = R ¹¹² = R ¹¹³ = R ¹¹⁴ = R ¹¹⁵ = R ¹¹⁶ = R ¹¹⁷ = R ¹¹⁸ = R ¹¹⁹ = R ¹²⁰ = R ¹²¹ = R ¹²² = R ¹²³ = R ¹²⁴ = R ¹²⁵ = R ¹²⁶ = R ¹²⁷ = R ¹²⁸ = R ¹²⁹ = R ¹³⁰ = R ¹³¹ = R ¹³² = R ¹³³ = R ¹³⁴ = R ¹³⁵ = R ¹³⁶ = R ¹³⁷ = R ¹³⁸ = R ¹³⁹ = R ¹⁴⁰ = R ¹⁴¹ = R ¹⁴² = R ¹⁴³ = R ¹⁴⁴ = R ¹⁴⁵ = R ¹⁴⁶ = R ¹⁴⁷ = R ¹⁴⁸ = R ¹⁴⁹ = R ¹⁵⁰ = R ¹⁵¹ = R ¹⁵² = R ¹⁵³ = R ¹⁵⁴ = R ¹⁵⁵ = R ¹⁵⁶ = R ¹⁵⁷ = R ¹⁵⁸ = R ¹⁵⁹ = R ¹⁶⁰ = R ¹⁶¹ = R ¹⁶² = R ¹⁶³ = R ¹⁶⁴ = R ¹⁶⁵ = R ¹⁶⁶ = R ¹⁶⁷ = R ¹⁶⁸ = R ¹⁶⁹ = R ¹⁷⁰ = R ¹⁷¹ = R ¹⁷² = R ¹⁷³ = R ¹⁷⁴ = R ¹⁷⁵ = R ¹⁷⁶ = R ¹⁷⁷ = R ¹⁷⁸ = R ¹⁷⁹ = R ¹⁸⁰ = R ¹⁸¹ = R ¹⁸² = R ¹⁸³ = R ¹⁸⁴ = R ¹⁸⁵ = R ¹⁸⁶ = R ¹⁸⁷ = R ¹⁸⁸ = R ¹⁸⁹ = R ¹⁹⁰ = R ¹⁹¹ = R ¹⁹² = R ¹⁹³ = R ¹⁹⁴ = R ¹⁹⁵ = R ¹⁹⁶ = R ¹⁹⁷ = R ¹⁹⁸ = R ¹⁹⁹ = R ²⁰⁰ = R ²⁰¹ = R ²⁰² = R ²⁰³ = R ²⁰⁴ = R ²⁰⁵ = R ²⁰⁶ = R ²⁰⁷ = R ²⁰⁸ = R ²⁰⁹ = R ²¹⁰ = R ²¹¹ = R ²¹² = R ²¹³ = R ²¹⁴ = R ²¹⁵ = R ²¹⁶ = R ²¹⁷ = R ²¹⁸ = R ²¹⁹ = R ²²⁰ = R ²²¹ = R ²²² = R ²²³ = R ²²⁴ = R ²²⁵ = R ²²⁶ = R ²²⁷ = R ²²⁸ = R ²²⁹ = R ²³⁰ = R ²³¹ = R ²³² = R ²³³ = R ²³⁴ = R ²³⁵ = R ²³⁶ = R ²³⁷ = R ²³⁸ = R ²³⁹ = R ²⁴⁰ = R ²⁴¹ = R ²⁴² = R ²⁴³ = R ²⁴⁴ = R ²⁴⁵ = R ²⁴⁶ = R ²⁴⁷ = R ²⁴⁸ = R ²⁴⁹ = R ²⁵⁰ = R ²⁵¹ = R ²⁵² = R ²⁵³ = R ²⁵⁴ = R ²⁵⁵ = R ²⁵⁶ = R ²⁵⁷ = R ²⁵⁸ = R ²⁵⁹ = R ²⁶⁰ = R ²⁶¹ = R ²⁶² = R ²⁶³ = R ²⁶⁴ = R ²⁶⁵ = R ²⁶⁶ = R ²⁶⁷ = R ²⁶⁸ = R ²⁶⁹ = R ²⁷⁰ = R ²⁷¹ = R ²⁷² = R ²⁷³ = R ²⁷⁴ = R ²⁷⁵ = R ²⁷⁶ = R ²⁷⁷ = R ²⁷⁸ = R ²⁷⁹ = R ²⁸⁰ = R ²⁸¹ = R ²⁸² = R ²⁸³ = R ²⁸⁴ = R ²⁸⁵ = R ²⁸⁶ = R ²⁸⁷ = R ²⁸⁸ = R ²⁸⁹ = R ²⁹⁰ = R ²⁹¹ = R ²⁹² = R ²⁹³ = R ²⁹⁴ = R ²⁹⁵ = R ²⁹⁶ = R ²⁹⁷ = R ²⁹⁸ = R ²⁹⁹ = R ³⁰⁰ = R ³⁰¹ = R ³⁰² = R ³⁰³ = R ³⁰⁴ = R ³⁰⁵ = R ³⁰⁶ = R ³⁰⁷ = R ³⁰⁸ = R ³⁰⁹ = R ³¹⁰ = R ³¹¹ = R ³¹² = R ³¹³ = R ³¹⁴ = R ³¹⁵ = R ³¹⁶ = R ³¹⁷ = R ³¹⁸ = R ³¹⁹ = R ³²⁰ = R ³²¹ = R ³²² = R ³²³ = R ³²⁴ = R ³²⁵ = R ³²⁶ = R ³²⁷ = R ³²⁸ = R ³²⁹ = R ³³⁰ = R ³³¹ = R ³³² = R ³³³ = R ³³⁴ = R ³³⁵ = R ³³⁶ = R ³³⁷ = R ³³⁸ = R ³³⁹ = R ³⁴⁰ = R ³⁴¹ = R ³⁴² = R ³⁴³ = R ³⁴⁴ = R ³⁴⁵ = R ³⁴⁶ = R ³⁴⁷ = R ³⁴⁸ = R ³⁴⁹ = R ³⁵⁰ = R ³⁵¹ = R ³⁵² = R ³⁵³ = R ³⁵⁴ = R ³⁵⁵ = R ³⁵⁶ = R ³⁵⁷ = R ³⁵⁸ = R ³⁵⁹ = R ³⁶⁰ = R ³⁶¹ = R ³⁶² = R ³⁶³ = R ³⁶⁴ = R ³⁶⁵ = R ³⁶⁶ = R ³⁶⁷ = R ³⁶⁸ = R ³⁶⁹ = R ³⁷⁰ = R ³⁷¹ = R ³⁷² = R ³⁷³ = R ³⁷⁴ = R ³⁷⁵ = R ³⁷⁶ = R ³⁷⁷ = R ³⁷⁸ = R ³⁷⁹ = R ³⁸⁰ = R ³⁸¹ = R ³⁸² = R ³⁸³ = R ³⁸⁴ = R ³⁸⁵ = R ³⁸⁶ = R ³⁸⁷ = R ³⁸⁸ = R ³⁸⁹ = R ³⁹⁰ = R ³⁹¹ = R ³⁹² = R ³⁹³ = R ³⁹⁴ = R ³⁹⁵ = R ³⁹⁶ = R ³⁹⁷ = R ³⁹⁸ = R ³⁹⁹ = R ⁴⁰⁰ = R ⁴⁰¹ = R ⁴⁰² = R ⁴⁰³ = R ⁴⁰⁴ = R ⁴⁰⁵ = R ⁴⁰⁶ = R ⁴⁰⁷ = R ⁴⁰⁸ = R ⁴⁰⁹ = R ⁴¹⁰ = R ⁴¹¹ = R ⁴¹² = R ⁴¹³ = R ⁴¹⁴ = R ⁴¹⁵ = R ⁴¹⁶ = R ⁴¹⁷ = R ⁴¹⁸ = R ⁴¹⁹ = R ⁴²⁰ = R ⁴²¹ = R ⁴²² = R ⁴²³ = R ⁴²⁴ = R ⁴²⁵ = R ⁴²⁶ = R ⁴²⁷ = R ⁴²⁸ = R ⁴²⁹ = R ⁴³⁰ = R ⁴³¹ = R ⁴³² = R ⁴³³ = R ⁴³⁴ = R ⁴³⁵ = R ⁴³⁶ = R ⁴³⁷ = R ⁴³⁸ = R ⁴³⁹ = R ⁴⁴⁰ = R ⁴⁴¹ = R ⁴⁴² = R ⁴⁴³ = R ⁴⁴⁴ = R ⁴⁴⁵ = R ⁴⁴⁶ = R ⁴⁴⁷ = R ⁴⁴⁸ = R ⁴⁴⁹ = R ⁴⁵⁰ = R ⁴⁵¹ = R ⁴⁵² = R ⁴⁵³ = R ⁴⁵⁴ = R ⁴⁵⁵ = R ⁴⁵⁶ = R ⁴⁵⁷ = R ⁴⁵⁸ = R ⁴⁵⁹ = R ⁴⁶⁰ = R ⁴⁶¹ = R ⁴⁶² = R ⁴⁶³ = R ⁴⁶⁴ = R ⁴⁶⁵ = R ⁴⁶⁶ = R ⁴⁶⁷ = R ⁴⁶⁸ = R ⁴⁶⁹ = R ⁴⁷⁰ = R ⁴⁷¹ = R ⁴⁷² = R ⁴⁷³ = R ⁴⁷⁴ = R ⁴⁷⁵ = R ⁴⁷⁶ = R ⁴⁷⁷ = R ⁴⁷⁸ = R ⁴⁷⁹ = R ⁴⁸⁰ = R ⁴⁸¹ = R ⁴⁸² = R ⁴⁸³ = R ⁴⁸⁴ = R ⁴⁸⁵ = R ⁴⁸⁶ = R ⁴⁸⁷ = R ⁴⁸⁸ = R ⁴⁸⁹ = R ⁴⁹⁰ = R ⁴⁹¹ = R ⁴⁹² = R ⁴⁹³ = R ⁴⁹⁴ = R ⁴⁹⁵ = R ⁴⁹⁶ = R ⁴⁹⁷ = R ⁴⁹⁸ = R ⁴⁹⁹ = R ⁵⁰⁰ = R ⁵⁰¹ = R ⁵⁰² = R ⁵⁰³ = R ⁵⁰⁴ = R ⁵⁰⁵ = R ⁵⁰⁶ = R ⁵⁰⁷ = R ⁵⁰⁸ = R ⁵⁰⁹ = R ⁵¹⁰ = R ⁵¹¹ = R ⁵¹² = R ⁵¹³ = R ⁵¹⁴ = R ⁵¹⁵ = R ⁵¹⁶ = R ⁵¹⁷ = R ⁵¹⁸ = R ⁵¹⁹ = R ⁵²⁰ = R ⁵²¹ = R ⁵²² = R ⁵²³ = R ⁵²⁴ = R ⁵²⁵ = R ⁵²⁶ = R ⁵²⁷ = R ⁵²⁸ = R ⁵²⁹ = R ⁵³⁰ = R ⁵³¹ = R ⁵³² = R ⁵³³ = R ⁵³⁴ = R ⁵³⁵ = R ⁵³⁶ = R ⁵³⁷ = R ⁵³⁸ = R ⁵³⁹ = R ⁵⁴⁰ = R ⁵⁴¹ = R ⁵⁴² = R ⁵⁴³ = R ⁵⁴⁴ = R ⁵⁴⁵ = R ⁵⁴⁶ = R ⁵⁴⁷ = R ⁵⁴⁸ = R ⁵⁴⁹ = R ⁵⁵⁰ = R ⁵⁵¹ = R ⁵⁵² = R ⁵⁵³ = R ⁵⁵⁴ = R ⁵⁵⁵ = R ⁵⁵⁶ = R ⁵⁵⁷ = R ⁵⁵⁸ = R ⁵⁵⁹ = R ⁵⁶⁰ = R ⁵⁶¹ = R ⁵⁶² = R ⁵⁶³ = R ⁵⁶⁴ = R ⁵⁶⁵ = R ⁵⁶⁶ = R ⁵⁶⁷ = R ⁵⁶⁸ = R ⁵⁶⁹ = R ⁵⁷⁰ = R ⁵⁷¹ = R ⁵⁷² = R ⁵⁷³ = R ⁵⁷⁴ = R ⁵⁷⁵ = R ⁵⁷⁶ = R ⁵⁷⁷ = R ⁵⁷⁸ = R ⁵⁷⁹ = R ⁵⁸⁰ = R ⁵⁸¹ = R ⁵⁸² = R ⁵⁸³ = R ⁵⁸⁴ = R ⁵⁸⁵ = R ⁵⁸⁶ = R ⁵⁸⁷ = R ⁵⁸⁸ = R ⁵⁸⁹ = R ⁵⁹⁰ = R ⁵⁹¹ = R ⁵⁹² = R ⁵⁹³ = R ⁵⁹⁴ = R ⁵⁹⁵ = R ⁵⁹⁶ = R ⁵⁹⁷ = R ⁵⁹⁸ = R ⁵⁹⁹ = R ⁶⁰⁰ = R ⁶⁰¹ = R ⁶⁰² = R ⁶⁰³ = R ⁶⁰⁴ = R ⁶⁰⁵ = R ⁶⁰⁶ = R ⁶⁰⁷ = R ⁶⁰⁸ = R ⁶⁰⁹ = R ⁶¹⁰ = R ⁶¹¹ = R ⁶¹² = R ⁶¹³ = R ⁶¹⁴ = R ⁶¹⁵ = R ⁶¹⁶ = R ⁶¹⁷ = R ⁶¹⁸ = R ⁶¹⁹ = R ⁶²⁰ = R ⁶²¹ = R ⁶²² = R ⁶²³ = R ⁶²⁴ = R ⁶²⁵ = R ⁶²⁶ = R ⁶²⁷ = R ⁶²⁸ = R ⁶²⁹ = R ⁶³⁰ = R ⁶³¹ = R ⁶³² = R ⁶³³ = R ⁶³⁴ = R ⁶³⁵ = R ⁶³⁶ = R ⁶³⁷ = R ⁶³⁸ = R ⁶³⁹ = R ⁶⁴⁰ = R ⁶⁴¹ = R ⁶⁴² = R ⁶⁴³ = R ⁶⁴⁴ = R ⁶⁴⁵ = R ⁶⁴⁶ = R ⁶⁴⁷ = R ⁶⁴⁸ = R ⁶⁴⁹ = R ⁶⁵⁰ = R ⁶⁵¹ = R ⁶⁵² = R ⁶⁵³ = R ⁶⁵⁴ = R ⁶⁵⁵ = R ⁶⁵⁶ = R ⁶⁵⁷ = R ⁶⁵⁸ = R ⁶⁵⁹ = R ⁶⁶⁰ = R ⁶⁶¹ = R ⁶⁶² = R ⁶⁶³ = R ⁶⁶⁴ = R ⁶⁶⁵ = R ⁶⁶⁶ = R ⁶⁶⁷ = R ⁶⁶⁸ = R ⁶⁶⁹ = R ⁶⁷⁰ = R ⁶⁷¹ = R ⁶⁷² = R ⁶⁷³ = R ⁶⁷⁴ = R ⁶⁷⁵ = R ⁶⁷⁶ = R ⁶⁷⁷ = R ⁶⁷⁸ = R ⁶⁷⁹ = R ⁶⁸⁰ = R ⁶⁸¹ = R ⁶⁸² = R ⁶⁸³ = R ⁶⁸⁴ = R ⁶⁸⁵ = R ⁶⁸⁶ = R ⁶⁸⁷ = R ⁶⁸⁸ = R ⁶⁸⁹ = R ⁶⁹⁰ = R ⁶⁹¹ = R ⁶⁹² = R ⁶⁹³ = R ⁶⁹⁴ = R ⁶⁹⁵ = R ⁶⁹⁶ = R ⁶⁹⁷ = R ⁶⁹⁸ = R ⁶⁹⁹ = R ⁷⁰⁰ = R ⁷⁰¹ = R ⁷⁰² = R ⁷⁰³ = R ⁷⁰⁴ = R ⁷⁰⁵ = R ⁷⁰⁶ = R ⁷⁰⁷ = R ⁷⁰⁸ = R ⁷⁰⁹ = R ⁷¹⁰ = R ⁷¹¹ = R ⁷¹² = R ⁷¹³ = R ⁷¹⁴ = R ⁷¹⁵ = R ⁷¹⁶ = R ⁷¹⁷ = R ⁷¹⁸ = R ⁷¹⁹ = R ⁷²⁰ = R ⁷²¹ = R ⁷²² = R ⁷²³ = R ⁷²⁴ = R ⁷²⁵ = R ⁷²⁶ = R ⁷²⁷ = R ⁷²⁸ = R ⁷²⁹ = R ⁷³⁰ = R ⁷³¹ = R ⁷³² = R ⁷³³ = R ⁷³⁴ = R ⁷³⁵ = R ⁷³⁶ = R ⁷³⁷ = R ⁷³⁸ = R ⁷³⁹ = R ⁷⁴⁰ = R ⁷⁴¹ = R ⁷⁴² = R ⁷⁴³ = R ⁷⁴⁴ = R ⁷⁴⁵ = R ⁷⁴⁶ = R ⁷⁴⁷ = R ⁷⁴⁸ = R ⁷⁴⁹ = R ⁷⁵⁰ = R ⁷⁵¹ = R ⁷⁵² = R ⁷⁵³ = R ⁷⁵⁴ = R ⁷⁵⁵ = R ⁷⁵⁶ = R ⁷⁵⁷ = R ⁷⁵⁸ = R ⁷⁵⁹ = R ⁷⁶⁰ = R ⁷⁶¹ = R ⁷⁶² = R ⁷⁶³ = R ⁷⁶⁴ = R ⁷⁶⁵ = R ⁷⁶⁶ = R ⁷⁶⁷ = R ⁷⁶⁸ = R ⁷⁶⁹ = R ⁷⁷⁰ = R ⁷⁷¹ = R ⁷⁷² = R ⁷⁷³ = R ⁷⁷⁴ = R ⁷⁷⁵ = R ⁷⁷⁶ = R ⁷⁷⁷ = R ⁷⁷⁸ = R ⁷⁷⁹ = R ⁷⁸⁰ = R ⁷⁸¹ = R ⁷⁸² = R ⁷⁸³ = R ⁷⁸⁴ = R ⁷⁸⁵ = R ⁷⁸⁶ = R ⁷⁸⁷ = R ⁷⁸⁸ = R ⁷⁸⁹ = R ⁷⁹⁰ = R ⁷⁹¹ = R ⁷⁹² = R ⁷⁹³ = R ⁷⁹⁴ = R ⁷⁹⁵ = R ⁷⁹⁶ = R ⁷⁹⁷ = R ⁷⁹⁸ = R ⁷⁹⁹ = R ⁸⁰⁰ = R ⁸⁰¹ = R ⁸⁰² = R ⁸⁰³ = R ⁸⁰⁴ = R ⁸⁰⁵ = R ⁸⁰⁶ = R ⁸⁰⁷ = R ⁸⁰⁸ = R ⁸⁰⁹ = R ⁸¹⁰ = R ⁸¹¹ = R ⁸¹² = R ⁸¹³ = R ⁸¹⁴ = R ⁸¹⁵ = R ⁸¹⁶ = R ⁸¹⁷ = R ⁸¹⁸ = R ⁸¹⁹ = R ⁸²⁰ = R ⁸²¹ = R ⁸²² = R ⁸²³ = R ⁸²⁴ = R ⁸²⁵ = R ⁸²⁶ = R ⁸²⁷ = R ⁸²⁸ = R ⁸²⁹ = R ⁸³⁰ = R ⁸³¹ = R ⁸³² = R ⁸³³ = R ⁸³⁴ = R ⁸³⁵ = R ⁸³⁶ = R ⁸³⁷ = R ⁸³⁸ = R ⁸³⁹ = R ⁸⁴⁰ = R ⁸⁴¹ = R ⁸⁴² = R ⁸⁴³ = R ⁸⁴⁴ = R ⁸⁴⁵ = R ⁸⁴⁶ = R ⁸⁴⁷ = R ⁸⁴⁸ = R ⁸⁴⁹ = R ⁸⁵⁰ = R ⁸⁵¹ = R ⁸⁵² = R ⁸⁵³ = R ⁸⁵⁴ = R ⁸⁵⁵ = R ⁸⁵⁶ = R ⁸⁵⁷ = R ⁸⁵⁸ = R ⁸⁵⁹ = R ⁸⁶⁰ = R ⁸⁶¹ = R ⁸⁶² = R ⁸⁶³ = R ⁸⁶⁴ = R ⁸⁶⁵ = R ⁸⁶⁶ = R ⁸⁶⁷ = R ⁸⁶⁸ = R ⁸⁶⁹ = R ⁸⁷⁰ = R ⁸⁷¹ = R ⁸⁷² = R ⁸⁷³ = R ⁸⁷⁴ = R ⁸⁷⁵ = R ⁸⁷⁶ = R ⁸⁷⁷ = R ⁸⁷⁸ = R ⁸⁷⁹ = R ⁸⁸⁰ = R ⁸⁸¹ = R ⁸⁸² = R ⁸⁸³ = R ⁸⁸⁴ = R ⁸⁸⁵ = R ⁸⁸⁶ = R ⁸⁸⁷ = R ⁸⁸⁸ = R ⁸⁸⁹ = R ⁸⁹⁰ = R ⁸⁹¹ = R ⁸⁹² = R ⁸⁹³ = R ⁸⁹⁴ = R ⁸⁹⁵ = R ⁸⁹⁶ = R ⁸⁹⁷ = R ⁸⁹⁸ = R ⁸⁹⁹ = R ⁹⁰⁰ = R ⁹⁰¹ = R ⁹⁰² = R ⁹⁰³ = R ⁹⁰⁴ = R ⁹⁰⁵ = R ⁹⁰⁶ = R ⁹⁰⁷ = R ⁹⁰⁸ = R ⁹⁰⁹ = R ⁹¹⁰ = R ⁹¹¹ = R ⁹¹² = R ⁹¹³ = R ⁹¹⁴ = R ⁹¹⁵ = R ⁹¹⁶ = R ⁹¹⁷ = R ⁹¹⁸ = R ⁹¹⁹ = R ⁹²⁰ = R ⁹²¹ = R ⁹²² = R ⁹²³ = R ⁹²⁴ = R ⁹²⁵ = R ⁹²⁶ = R ⁹²⁷ = R ⁹²⁸ = R ⁹²⁹ = R ⁹³⁰ = R ⁹³¹ = R ⁹³² = R ⁹³³ = R ⁹³⁴ = R ⁹³⁵ = R ⁹³⁶ = R ⁹³⁷ = R ⁹³⁸ = R ⁹³⁹ = R ⁹⁴⁰ = R ⁹⁴¹ = R ⁹⁴² = R ⁹⁴³ = R ⁹⁴⁴ = R ⁹⁴⁵ = R ⁹⁴⁶ = R ⁹⁴⁷ = R ⁹⁴⁸ = R ⁹⁴⁹ = R ⁹⁵⁰ = R ⁹⁵¹ = R ⁹⁵² = R ⁹⁵³ = R ⁹⁵⁴ = R ⁹⁵⁵ = R ⁹⁵⁶ = R ⁹⁵⁷ = R ⁹⁵⁸ = R ⁹⁵⁹ = R ⁹⁶⁰ = R ⁹⁶¹ = R ⁹⁶² = R ⁹⁶³ = R ⁹⁶⁴ = R ⁹⁶⁵ = R ⁹⁶⁶ = R ⁹⁶⁷ = R ⁹⁶⁸ = R ⁹⁶⁹ = R ⁹⁷⁰ = R ⁹⁷¹ = R ⁹⁷² = R ⁹⁷³ = R ⁹⁷⁴ = R ⁹⁷⁵ = R ⁹⁷⁶ = R ⁹⁷⁷ = R ⁹⁷⁸ = R ⁹⁷⁹ = R ⁹⁸⁰ = R ⁹⁸¹ = R ⁹⁸² = R ⁹⁸³ = R ⁹⁸⁴ = R ⁹⁸⁵ = R ⁹⁸⁶ = R ⁹⁸⁷ = R ⁹⁸⁸ = R ⁹⁸⁹ = R ⁹⁹⁰ = R ⁹⁹¹ = R ⁹⁹² = R ⁹⁹³ = R ⁹⁹⁴ = R ⁹⁹⁵ = R ⁹⁹⁶ = R ⁹⁹⁷ = R ⁹⁹⁸ = R ⁹⁹⁹ = R ¹⁰⁰⁰ = R ¹⁰⁰¹ = R ¹⁰⁰² = R ¹⁰⁰³ = R ¹⁰⁰⁴ = R ¹⁰⁰⁵ = R ¹⁰⁰⁶ = R ¹⁰⁰⁷ = R ¹⁰⁰⁸ = R ¹⁰⁰⁹ = R ¹⁰¹⁰ = R ¹⁰¹¹ = R ¹⁰¹² = R ¹⁰¹³ = R ¹⁰¹⁴ = R ¹⁰¹⁵ = R ¹⁰¹⁶ = R ¹⁰¹⁷ = R ¹⁰¹⁸ = R ¹⁰¹⁹ = R ¹⁰²⁰ = R ¹⁰²¹ = R ¹⁰²² = R ¹⁰²³ = R ¹⁰²⁴ = R ¹⁰²⁵ = R ¹⁰²⁶ = R ¹⁰²⁷ = R ¹⁰²⁸ = R ¹⁰²⁹ = R ¹⁰³⁰ = R ¹⁰³¹ = R ¹⁰³² = R ¹⁰³³ = R ¹⁰³⁴ = R ¹⁰³⁵ = R ¹⁰³⁶ = R ¹⁰³⁷ = R ¹⁰³⁸ = R ¹⁰³⁹ = R ¹⁰⁴⁰ = R ¹⁰⁴¹ = R ¹⁰⁴² = R ¹⁰⁴³ = R ¹⁰⁴⁴ = R ¹⁰⁴⁵ = R ¹⁰⁴⁶ = R ¹⁰⁴⁷ = R ¹⁰⁴⁸ = R ¹⁰⁴⁹ = R ¹⁰⁵⁰ = R ¹⁰⁵¹ = R ¹⁰⁵² = R ¹⁰⁵³ = R ¹⁰⁵⁴ = R ¹⁰⁵⁵ = R ¹⁰⁵⁶ = R ¹⁰⁵⁷ = R ¹⁰⁵⁸ = R ¹⁰⁵⁹ = R ¹⁰⁶⁰ = R ¹⁰⁶¹ = R ¹⁰⁶² = R ¹⁰⁶³ = R ¹⁰⁶⁴ = R ¹⁰⁶⁵ = R ¹⁰⁶⁶ = R ¹⁰⁶⁷ = R ¹⁰⁶⁸						

TABLE III
 Microanalyses *N*-imidazolides triazolides

Product	Molecular Formula	Calculated					Found				
		C	H	N	P	S	C	H	N	P	S
CH ₃ SO ₂ Im	C ₄ H ₆ N ₂ O ₂ S (146.2)	32.9	4.1	19.2	—	21.9	33.1	4.0	19.4	—	21.8
(C ₂ H ₅ O) ₂ P(O)Im	C ₇ H ₁₃ N ₂ O ₃ P (204.2)	41.2	6.4	13.7	15.2	—	41.0	6.4	13.9	15.2	—
(C ₃ H ₇ O) ₂ P(O)Im	C ₉ H ₁₅ N ₂ O ₃ P (232.2)	46.6	6.5	12.1	13.3	—	46.6	6.3	12.0	13.1	—
<i>t</i> -Bu(MeO)P(O)Im	C ₈ H ₁₅ N ₂ O ₂ P (202.2)	47.5	7.5	13.9	15.3	—	47.2	7.4	13.9	15.2	—
(C ₂ H ₅ O) ₂ P(S)Im	C ₇ H ₁₃ N ₂ O ₂ PS (220.2)	38.2	6.0	12.7	14.1	14.1	38.1	6.0	12.7	14.2	14.7
<i>t</i> -Bu(Ph)PIm	C ₁₃ H ₁₇ N ₂ P (232.3)	67.2	7.4	12.1	13.3	—	67.2	7.0	12.0	13.2	—
(C ₆ H ₅) ₂ PIm	C ₁₅ H ₁₃ N ₂ P (252.3)	71.4	5.2	11.1	12.3	—	71.2	5.0	11.0	12.2	—
Me ₃ SiOSO ₂ Im	C ₆ H ₁₂ N ₂ O ₃ SSi (221.1)	32.6	5.8	12.7	—	14.5	32.4	5.8	12.5	—	14.3
C ₆ H ₅ P(O)Im ₂	C ₁₂ H ₁₁ N ₄ OP (258.3)	55.8	4.3	21.7	12.0	—	55.7	4.2	21.8	12.1	—
<i>t</i> -BuPIm ₂	C ₁₀ H ₁₅ N ₄ P (222.2)	54.1	6.8	25.2	14.0	—	54.0	6.8	25.2	14.1	—
CH ₃ SO ₂ Tr	C ₃ H ₅ N ₃ O ₂ S (147.2)	24.5	3.4	28.5	—	21.7	24.6	3.6	28.6	—	21.7
(C ₂ H ₅ O) ₂ P(O)Tr	C ₆ H ₁₂ N ₃ O ₃ P (206.0)	35.0	5.8	20.4	15.1	—	35.1	5.9	20.5	15.1	—
(C ₂ H ₅ O) ₂ P(S)Tr	C ₆ H ₁₂ N ₃ O ₂ PS (220.0)	32.7	5.5	19.1	14.1	14.6	32.7	5.4	19.0	14.1	14.5
(C ₂ H ₅ O) ₂ PTr	C ₆ H ₁₂ N ₃ O ₂ P (190.0)	37.9	6.3	22.1	16.3	—	37.9	6.2	22.0	16.2	—



REFERENCES

1. W. Dąbkowski, A. Łopusiński, J. Michalski and Cz. Radziejewski, *Phosphorus and Sulfur*, **8**, 375 (1980).
2. W. Dąbkowski, J. Michalski, Cz. Radziejewski and Z. Skrzypczyński, *Chem. Ber.*, **115**, 1636 (1982).
3. W. Dąbkowski, J. Michalski and Z. Skrzypczyński, *J. Chem. Soc., Chem. Commun.*, **1982** 1260.
4. N. Katagin, K. Itakura and S. A. Narang, *J. Am. Chem. Soc.*, **97** 7332 (1975).
5. Yu. A. Berlin, O. G. Chakhmakhcheva, V. A. Efimov, M. N. Kolosov and V. G. Korobko, *Tetrahedron Lett.*, **1973**, 1353.
6. F. Cramer, H. Schaller and H. A. Staab, *Chem. Ber.*, **94**, 1612 (1961).
7. F. Ramirez, H. Okazaki and J. F. Marecek, *Synthesis*, **1975**, 637.
8. L. Birkofer, W. Gilgenberg and A. Ritter, *Angew. Chem.*, **73**, 143 (1961).
9. ³¹P-NMR (CDCl₃): δ = +53.581, *J*_{P-S} = 839.8 Hz.
10. P. Baumgarten, *Ber. Dtsch. Chem. Ges.*, **59**, 1166 (1926).
11. In the patent literature, C. A. 9088d, 1963 the adduct of imidazol and sulfurtrioxide is described as a sirup.
12. ¹H-NMR (CDCl₃) imidazole ring 7.9 (s, 1 H); 9.1 (s, 1 H); 9.3 (s, 1 H); 13.4 (s, 1 H) C₃H₄N₂O₃S (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 (CH₃COCH₃/CH₂Cl₂). Yield of recrystallized product 91%.
13. S. T. Abbott, S. T. Jones, S. A. Weinman, F. M. Bockhoff, F. W. McLafferty and J. R. Knowles, *J. Am. Chem. Soc.* **101** 4323 (1979).