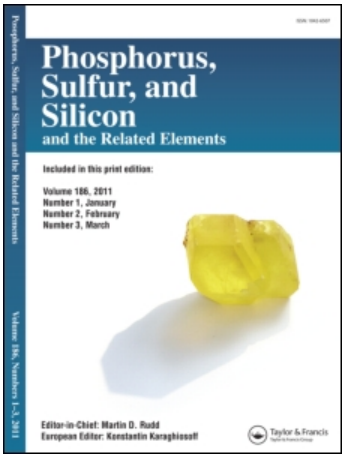

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Communication

A MILD CONVENIENT SYNTHESIS OF HETEROCYCLIC TRIPHENYLPHOSPHINE IMINES

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A series of heterocyclic phosphine imines (1,3,5-triazines, pyrazines, pyridines, furazans and furoxans) have been readily prepared by direct action of *N*-trimethylsilyl-*P*,*P*,*P*-triphenylphosphine imines on chloro- or nitroderivatives.

Key words: Triphenylphosphine imines; heterocycles; trimethylsilyltriphenylphosphine imine.

Phosphine imines are widely used synthetic equivalents in various syntheses. New heterocyclic compounds (quinolines, tetrazoles, oxazoles, pyrazines, etc), hardly accessible amines, phosphorheterocycles have been received by means of these synthetic equivalents.[1,2] Phosphine imines are also used for formation of C=N bonds.[3] Heterocyclic phosphine imines could in turn serve as starting compounds for such syntheses, however, their utilization is restricted owing to the lack of effective methods for their preparation.

The most common synthetic route to heterocyclic phosphine imines is the Staudinger reaction—the interaction of tertiary phosphines with organic azides.[1,4] However, this method is of limited applicability owing to the explosive nature of organic azides. Other methods of rare use are based on reaction of heterocyclic amines with various phosphorus compounds (Ph_3PCl_2, PCl_5, Oct_3PO, Ph_3PO).[1,4,5] But these methods require often hardly accessible activating reagents and complicated operations.

RESULTS AND DISCUSSION

Here we describe a simple one-pot method for the preparation of heterocyclic phosphine imines using a nucleophilic substitution with *N*-trimethyl-*P*,*P*,*P*-triphenylphosphine imine (**1**).[6] We could show that activated chloro- (**2**) and nitroderivatives (**3**) of heterocycles (triazine, pyrazine, pyridine, furazan and furoxan) and also picrylchloride treated with *N*-silylated phosphine imine (**1**) gave monosubstituted phosphine imines (**4**) (Scheme I). The yields of compounds obtained

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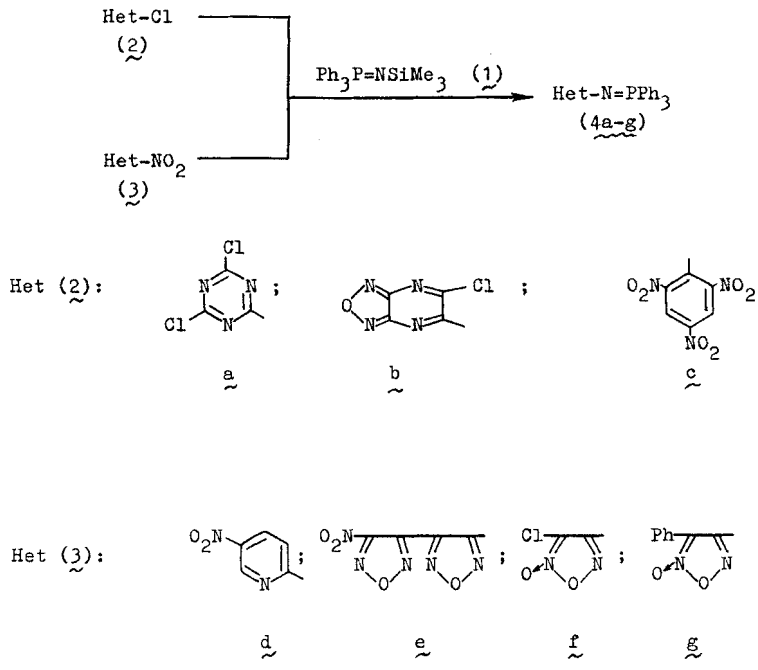

SCHEME I

are given in Table I. Lower yield e.g. for **4e-g** should be explained by occurrence of some side reactions.

It should be pointed out that our method is distinguished by mild conditions and has advantage in some cases over the well known Staudinger reaction used in preparation of monosubstituted phosphine imines. Thus, in the case of 2,4,6-trichloro-1,3,5-triazine the Staudinger reaction gave solely tris-triphenylphosphinimino derivatives,[4] whereas (**2b**) or (**3f**) decompose in reaction with sodium azide.

The important feature of this method is the formation of only monosubstituted phosphine imines even in cases when two or three groups could be substituted (**2a–c**, **3d–f**).

EXPERIMENTAL

The melting points are determined on Boetius apparatus and are uncorrected. The ^{13}C and ^{31}P NMR spectra were obtained on AM-300 Bruker at 75.5 and 121.5 MHz, respectively, in $CDCl_3$, solution with TMS and phosphoric acid as standards. The IR spectra were recorded on Specord spectrometer in KBr tablets.

Typical procedure. To a stirred solution of (**2**) or (**3**) in dichloromethane (amount of which depends on solubility of the substance) $Ph_3PNSiMe_3$ (1.5 fold excess) in dichloromethane was added. Temperatures and reaction times are shown in Table I. After termination of the reaction the mixture was washed with aq. $NaHCO_3$ (twice), H_2O (once) and dried ($MgSO_4$). The solvent was removed in vacuo and the residue chromatographed on a column of Silica gel (L 100/250 m, Chemapol) in 1:1 chloroform–carbon tetrachloride. The yields, spectral characteristics, elemental analysis data are given in Tables I and II.

TABLE I

Preparation and characterization of heterocyclic triphenylphosphine imines **4a–g**

Product	Time h	Temp. °C	Yield %	M.p. °C	Rf $\frac{CCl_4}{CHCl_3}$	Molecular Formula	Elemental analysis (%) Found / Calculated C	H	N	P	Cl
4a	0.5	18-25	68	208-210	0.58	$C_{21}H_{15}Cl_2N_4P$	58.99 / 59.31	3.22 / 3.56	12.88 / 13.17	7.01 / 7.28	16.93 / 16.67
4b	0.5	18-25	75	214-215	0.44	$C_{22}H_{15}ClN_5OP$	61.02 / 61.19	3.37 / 3.50	16.00 / 16.22	7.06 / 7.17	8.12 / 8.21
4c	0.5	18-25	84	184-185	0.42	$C_{24}H_{17}N_4O_6P$	58.87 / 59.02	3.42 / 3.51	11.39 / 11.47	6.23 / 6.34	
4d	0.5	18-25	60	212-213	0.07	$C_{23}H_{18}N_3O_2P$	69.17 / 69.17	4.49 / 4.54	10.37 / 10.52	7.70 / 7.75	
4e	1	0-10	21	117-118	0.50	$C_{22}H_{15}N_6O_4P$	57.39 / 57.65	3.29 / 3.30	18.34 / 18.34	6.90 / 6.76	
4f	4	0-10	30	129-130	0.27	$C_{20}H_{15}ClN_3O_2P$	60.52 / 60.69	3.68 / 3.82	10.86 / 10.62	7.72 / 7.83	8.81 / 8.96
4g	2	61 ($CHCl_3$)	44	168-169	0.36	$C_{26}H_{20}N_3O_2P$	71.45 / 71.39	4.62 / 4.61	9.30 / 9.61	7.13 / 7.08	

TABLE II

^{13}C and ^{31}P NMR data of compounds **4a–g**

Product	^{13}C, (ppm)	^{31}P (ppm)
4a	126.86, 128.64, 132.73, 133.10 (Ph-P); 169.17 (C-N); 170.08 (C-Cl)	18.37
4b	125.98, 129.12, 133.28, 133.43 (Ph-P); 149.86, 152.62 (C=N-O); 157.16 (C-Cl); 160.44 (C-N=P)	20.54
4c	128.36, 128.84, 132.17, 132.57 (Ph-P); 123.01 (CH(Ph)); 133.25 (C-N=P); 144.48 (p-), 145.08 (o-)	10.97
4d	128.26, 128.51, 132.11, 133.01 (Ph-P) 116.62, 131.78, 145.48 (CH(Py)), 135.23 (C-NO_2), 168.34 (C-N=P)	14.90
4e	126.87, 128.83, 132.75, 132.83 (Ph-P), 139.04, 139.67 (C-C), 158.25 (C-N=P), 159.33 (C-NO_2)	18.35
4f	127.33, 128.81, 132.75, 132.80 (Ph-P), 109.74 (C-Cl), 157.58 (C-N)	13.93
4g	126.10, 128.68, 132.46, 132.80 (P-Ph), 112.23 (C-Ph), 127.17, 128.08, 128.09, 129.28 (Ph-C), 158.68 (C-N)	18.78

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