An Improved Synthesis of 1*H*-1,2,4-Triazoles from *C*-Triphenylphosphinimino-hydrazones

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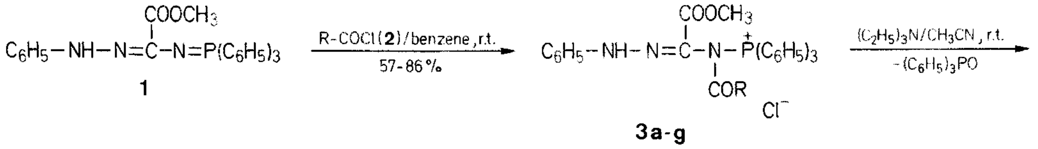
1-Phenyl-1*H*-1,2,4-triazoles **5a–h** are prepared in good yields by reaction of the triphenylphosphine imide **1** with acyl chlorides **2a–h** and subsequent base treatment of the intermediate phosphonium salts **3a–h**.

Phosphine imides like **1** have been occasionally reported[1], but little is known on their chemical behaviour. In a previous paper, we described the preparation of compound **1** and its reaction with aldehydes as an entry to 1*H*-1,2,4-triazoles[2]. We now wish to report that 1-phenyl-1*H*-1,2,4-triazoles are also formed by reacting the same phosphine imide **1** with acyl chlorides. The advantages of this new procedure are the milder conditions and the better yields. Furthermore, primary intermediates can be isolated, thus shedding light on the reaction mechanism.

Treatment of **1** with an excess of the acyl chloride **2** in benzene at room temperature led to the phosphonium salts **3**, which were usually isolated as crystalline compounds of analytical purity. The latter intermediates reacted with triethylamine in acetonitrile to afford the triazole derivatives **5** along with triphenylphosphine oxide. The intermediacy of the species **4** is a plausible mechanistic option in view of the



2-5	R	2-5	R
a	CH_3	e	$4\text{-}CH_3C_6H_4$
b	CH_2Cl	f	$4\text{-}CH_3OC_6H_4$
c	CH_3CHCl	g	$4\text{-}O_2NC_6H_4$
d	C_6H_5	h	$3,5\text{-}(NO_2)_2C_6H_3$

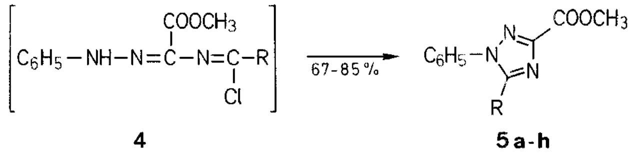


Table 1. Preparation of Phosphonium Chlorides **3**

3	Reaction Time [h]	Yield [%]	m.p. [°C][a]	Molecular Formula[b]	IR (Nujol) $[cm^{-1}]$	MS[c] m/e	^{1}H-NMR ($CDCl_3/TMS_{int}$) δ[ppm]
a	1	85	146-147	$C_{29}H_{27}ClN_3O_3P$ (532.0)	1745, 1685	496	2.38 (br. s, 3H); 3.58 (s, 3H); 7.1-7.8 (m, 20H)
b	0.5	86	138-139	$C_{29}H_{26}Cl_2N_3O_3P$ (566.5)	1760, 1685	530	3.52 (s, 3H); 4.50 (br. s, 2H); 7.1-7.8 (m, 20H)
c	2	84	140-141	$C_{30}H_{28}Cl_2N_3O_3P$ (580.50)	1745, 1690	544	1.75 (d, 3H, J = 7 Hz); 3.60 (s, 3H); 5.48 (br. s, 1H); 7.2-7.9 (m, 20H)
d	3	57	122-123	$C_{34}H_{29}ClN_3O_3P$ (594.1)	1750, 1670	558	3.47 (s, 3H); 7.1-7.9 (m, 25H)
e	12	62	124-125	$C_{35}H_{31}ClN_3O_3P$ (608.1)	1745, 1680	572	2.40 (s, 3H); 3.48 (s, 3H); 6.8-7.8 (m, 24H)
f	24	60	126-127	$C_{35}H_{31}ClN_3O_4P$ (624.1)	1745, 1670	588	3.45 (s, 3H); 3.82 (s, 3H); 6.68 (d, 2H); 7.1-7.8 (m, 22H)
g[d]	1	80	121-122	$C_{34}H_{28}ClN_4O_5P$ (639.1)	1750, 1675	603	3.50 (s, 3H); 7.1-8.2 (m, 24H)

[a] From chloroform/diisopropyl ether.
[b] Satisfactory microanalyses were obtained: C ±0.30, H ±0.25, N ±0.30.
[c] Measured by the FAB technique.
[d] ^{31}P-NMR ($CDCl_3/H_3PO_{4ext}$): δ = 28.0 ppm.

Table 2. Preparation of 1*H*-1,2,4-Triazoles **5**

5	Reaction Time [h]	Eluant	Yield [%]	m.p. [°C]	Molecular Formula[a] or Lit. m.p. [°C]	^{1}H-NMR ($CDCl_3/TMS_{int}$) δ[ppm]
a	12	tetrachloromethane/acetonitrile (2:1)	85	99[b]	101.5-102.5[4]	–
b	2	tetrachloromethane/acetonitrile (2:1)	78	62[c]	$C_{11}H_{10}ClN_3O_2$ (251.7)	4.08 (s, 3H); 4.74 (s, 2H); 7.62 (s, 5H)
c	8	tetrachloromethane/acetonitrile (2:1)	74	95[c]	$C_{12}H_{12}ClN_3O_2$ (265.7)	2.04 (d, 3H, J = 7 Hz); 4.06 (s, 3H); 5.08 (q, 1H, J = 7 Hz); 7.58 (s, 5H)
d	3	light petroleum/ethyl acetate (1:1)	82	160[b]	158-159[5]	–
e	12	light petroleum/ethyl acetate (1:1)	67	156[b]	$C_{17}H_{15}N_3O_2$ (293.3)	2.37 (s, 3H); 4.08 (s, 3H); 7.0-7.5 (m, 9H)
f	7	tetrachloromethane/acetonitrile (2:1)	85	143[b]	$C_{17}H_{15}N_3O_3$ (309.3)	3.82 (s, 3H); 4.05 (s, 3H); 6.7-7.6 (m, 9H)
g	3	benzene/ethyl acetate (1:1)	81	163[c]	162-163[2]	–
h[d]	–	–	–	239[e]	$C_{16}H_{11}N_5O_6$ (369.3)	3.98 (s, 3H); 7.60 (s, 5H); 8.61 (m, 2H); 8.90 (m, 1H)[f]

[a] Satisfactory microanalyses were obtained for the new compounds: C ±0.20, H ±0.20, N ±0.30.
[b] From diisopropyl ether/chloroform.
[c] From diisopropyl ether/methanol.
[d] See text.
[e] From acetone.
[f] In DMSO-d_6.

known formation of imidoyl chlorides upon reaction of phosphine imides with acyl chlorides[3]. In the present case, the nucleophilic participation of the hydrazone moiety accounts well for the conversion of **4** to the ring-closed products **5**. Unlike **3a–g**, compound **3h** could not be isolated owing to its high reactivity; in fact, the reaction of **1** with **2h** gave the final triazole **5h** directly.

It remains to be said that the phosphonium chlorides **3** can give **5** upon heating in the absence of triethylamine; however, in most cases, this thermal reaction proceeds slowly and is accompanied by tar formation. On the other hand, the conversion of **1** to **5** can also be effected following an one-pot procedure, without isolating the intermediates **3**, by addition of triethylamine to the benzene medium.

Phosphonium Chlorides 3; General Procedure:
A solution of compound **1** (1.1 mmol) and acyl chloride **2** (2.2 mmol) in dry benzene (50 ml) is stirred at room temperature for the time indicated in Table 1. The precipitate is collected by filtration and washed with a small quantity of benzene to afford practically pure **3** (Table 1).

Under the same conditions, compound **1** is reacted with **2h** during 2 h to give **5h** in 71 % yield.

1*H*-1,2,4-Triazoles 5; General Procedure:
A solution of phosphonium chloride **3** (2 mmol) and triethylamine (6 mmol) in acetonitrile (100 ml) is left at room temperature for the time given in Table 2. The solvent is removed under reduced pressure and the residue is taken with water and ether. The organic layer is dried over sodium sulphate, and the residue is chromatographed on a silica gel column to give triazole **5** (Table 2).

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