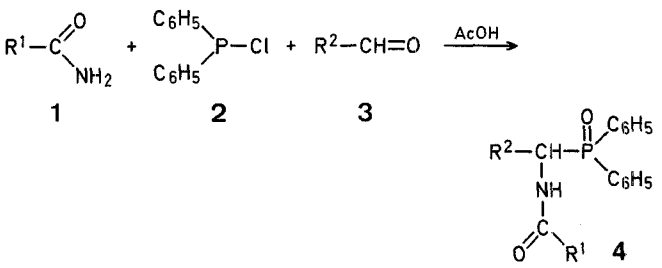
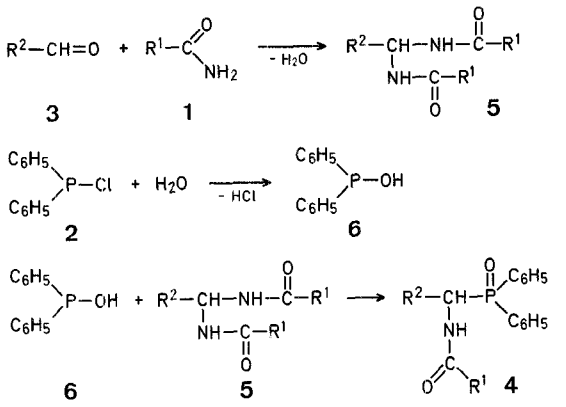
phosphinic acids. *N*-Substituted amides also reacted similarly to give *N*-alkyl-1-aminoalkanephosphonic and 1-aminoalkanephosphinic acids[4].

This paper describes a novel route for the synthesis of new *N*-acylated 1-aminoalkyl-diphenylphosphine oxides **4**, for which only few examples have been prepared so far[5]. Practically, the α-amidoalkylation is performed by treatment of a mixture of amide **1** and diphenylchlorophosphine (**2**) in acetic acid solution with aldehyde **3**.

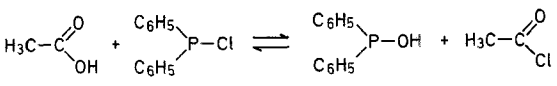


The products **4** are readily isolated by evaporation of the reaction mixtures after the condensation step to remove acetic acid, followed by treatment with methanol, and crystallization.

This reaction seems to involve initial formation of the intermediate **5**, followed by the reaction of **5** with the diphenylphosphinous acid (**6**) to give **4** and the starting amide **1**.



We have found that the *N*,*N*′-alkylidene or -arylidenebis-amides **5** can be employed as starting materials for the amidoalkylation of diphenylchlorophosphine **2** in acetic acid solution. Most likely this is due to the existence of an equilibrium between the diphenylchlorophosphine and acetic acid[6]:



and that **5** reacts with diphenylphosphinous acid (**6**) to give the *N*-acylated 1-aminoalkyl-diphenylphosphine oxide **4**, amide **1**, and acetyl chloride. Diphenylphosphinous acid, obtained by separate hydrolysis of **2** in acetic acid solution, also reacts with **5** to give the desired product **4**. This mechanistic proposal, which could be general for the amidoalkylation of trivalent phosphorus chlorides[1-4] is under investigation.

Although the yields of **4** are better than those obtained by the direct amidoalkylation, this second route, via bis-amides, is not recommended because it requires prior synthesis of **5** which is sometimes very difficult to obtain in the pure state[7]. The direct amidoalkylation appears to be a simpler procedure and affords

Synthesis of *N*-Acylated 1-Aminoalkyl-diphenylphosphine Oxides by Amidoalkylation of Diphenylchlorophosphine

Józef Oleksyszyn

Institute of Organic and Physical Chemistry, Technical University (Politechnika), 50-370 Wrocław, Wyb. Wyspiańskiego 27, Poland

We recently reported the direct α-amidoalkylation of the trivalent phosphorus chlorides with amides and carbonyl compounds[1,2,3]. This reaction represents a useful route for the preparation of the 1-aminoalkanephosphonic and 1-aminoalkane-

0039-7881/81/0632-0444 $ 03.00

Table. *N*-Acylated 1-Aminoalkyl-diphenylphosphine Oxides **4**

Product No.	R^1	R^2	Yield [%]	m.p. [°C]	Molecular formula[a]	I.R. (KBr) ν[cm^{-1}]	^{1}H-N.M.R. (solvent) δ[ppm]
4a	$ClCH_2$	*i*-C_3H_7	37	254–256°	$C_{18}H_{21}ClNO_2P$ (349.8)	3260, 3040, 2980, 2930, 1680, 1530, 1143, 1170, 1115	(F_3C—COOD): 0.78 (d, 3H); 0.93 (d, 3H); 2.1–1.4 (m, 1H); 3.85 (s, 2H); 6.9–5.1 (m, 1H); 7.2–7.9 (m, 10H)
4b	$ClCH_2$	*i*-C_3H_7—CH_2	35	227–229°	$C_{18}H_{23}ClNO_2P$ (363.8)	3210, 3050, 2980, 1680, 1540, 1435, 1175, 1120	(F_3C—COOD): 0.73 (d, 6H); 1.2–2.0 (m, 3H); 3.83 (s, 2H); 5.1–5.4 (m, 1H); 7.2–7.9 (m, 10H)
4c	$ClCH_2$	C_6H_5	60	309–311°	$C_{21}H_{19}ClNP_2P$ (383.8)	3210, 3050, 2940, 1675, 1540, 1430, 1235, 1175, 1115	(F_3C—COOD): 3.86 (s, 2H); 6.08 (d, 1H, J_{HP} = 7 Hz); 6.9–7.9 (m, 15H)
4d	CH_3	*i*-C_3H_7	48	243–245°	$C_{18}H_{22}NO_2P$ (312.3)	3280, 2980, 2930, 1675, 1520, 1435, 1375, 1285, 1175, 1115	($CDCl_3$): 1.20 (d, 3H); 1.30 (d, 3H); 2.2–2.6 (m, 4H); 5.3–5.6 (m, 1H); 7.7–8.3 (m, 10H); 8.82 (d, 1H, J_{HH} = 10 Hz)
4e	CH_3	*n*-C_3H_7	38	207–209°	$C_{18}H_{22}NO_2P$ (312.3)	3250, 3210, 3060, 2960, 2940, 1660, 1540, 1435, 1180, 1115	($CDCl_3$): 1.07 (t, 3H); 1.5–2.4 (m, 7H); 5.3–5.6 (m, 1H); 7.6–8.3 (m, 10H); 9.50 (d, 1H, J_{HH} = 10 Hz)
4f	CH_3	C_6H_5	63	308–310°	$C_{21}H_{20}NO_2P$ (349.3)	3240, 3210, 3070, 2940, 1660, 1540, 1490, 1430, 1360, 1285, 1180, 1115	(F_3C—COOD): 1.88 (s, 3H); 6.05 (d, 1H, J_{HP} = 6 Hz); 6.8–7.9 (m, 15H)
4g	C_2H_5	*i*-C_3H_7	43	233–235°	$C_{19}H_{24}NO_2P$ (326.3)	3280, 2980, 2940, 1670, 1520, 1435, 1290, 1210, 1175, 1115	($CDCl_3$): 1.1–1.6 (m, 9H); 2.3–2.7 (m, 3H); 5.2–5.5 (m, 1H); 7.6–8.4 (m, 10H)
4h	C_6H_5	*n*-C_3H_7	36	232–234°	$C_{23}H_{24}NO_2P$ (377.4)	3250, 3070, 2940, 1645, 1530, 1435, 1315, 1180	(F_3C—COOD): 0.70 (t, 3H); 1.1–1.5 (m, 2H); 1.5–2.0 (m, 2H); 5.2–4.5 (m, 1H); 7.0–8.2 (m, 15H)
4i	C_6H_5	*i*-C_3H_7	48	204–205°	$C_{23}H_{24}NO_2P$ (377.4)	3250, 3080, 2980, 2940, 1650, 1520, 1435, 1305, 1190	(F_3C—COOD): 0.74 (d, 3H, J_{HH} = 7 Hz); 0.89 (d, 3H, J_{HH} = 7 Hz); 1.8–2.3 (m, 1H); 4.9–5.1 (m, 1H); 7.1–7.9 (m, 15H)
4j	C_6H_5	CH_3	40	229–230°	$C_{21}H_{20}NO_2P$ (349.3)	3220, 3080, 1645, 1535, 1435, 1320, 1180	($CDCl_3$): 1.83 (dd, 3H, J_{HP} = 14 Hz); 7.7–8.0 (m, 1H); 7.4–8.3 (m, 10H); 9.13 (d, 1H, J_{HH} = 10 Hz)
4k	C_6H_5	*i*-C_3H_7—CH_2	35	245–246°	$C_{24}H_{26}NO_2P$ (377.4)	3260, 3060, 2950, 1640, 1525, 1430, 1315, 1180	($CDCl_3$): 1.18 (2d, 6H); 1.4–2.7 (m, 3H); 5.7–6.0 (m, 1H); 7.5–8.4 (m, 15H); 9.26 (d, 1H, J_{HH} = 10 Hz)

[a] Satisfactory microanalyses obtained: N ± 0.31, P ± 0.33, Cl ± 0.26.

satisfactory yields of products, as shown by the results summarized in the Table; however, it is limited to aldehydes and unsubstituted amides. Attempts to extend the reaction scope to include ketones and *N*-alkylamides were without success.

N-Acylated 1-Aminoalkyl-diphenylphosphine Oxides 4; General Procedure:

Freshly distilled aldehyde **3** (0.15 mol) is slowly added during 20 min to a stirred mixture of amide **1** (0.1 mol), diphenylchlorophosphine (**2**; 22 g, 0.1 mol) and glacial acetic acid (20 ml) (exothermic reaction with evolution of hydrogen chloride). The mixture is then heated under reflux for 40 min and volatile products are removed on a rotary evaporator under reduced pressure with heating on a boiling water bath. The oily residue is then dissolved in methanol (40–60 ml) and left for crystallization at −10 °C. After 1–3 h, the crystalline product is collected by filtration and recrystallized from ethanol. Yields, based on diphenylchlorophosphine, and spectral data of compounds obtained are given in Table.

Received: December 15, 1980

[1] J. Oleksyszyn, M. Soroka, J. Rachoń, *Chimia* **32**, 253 (1978).

[2] J. Oleksyszyn, R. Tyka, P. Mastalerz, *Synthesis* **1978**, 479.

[3] J. Oleksyszyn et al., Abstracts, International Symposium Phosphorus Chemistry Directed Towards Biology, Burzenin, Poland, September, 1979.

[4] J. Oleksyszyn, *Synthesis* **1980**, 722.

[5] K. A. Petrow, W. A. Chauzow, T. S. Erochina, *Usp. Khim.* **43**, 2045 (1974); *C.A.* **82**, 43486 (1975).

[6] N. A. Kardanov, N. N. Godovikov, M. J. Kabachnik, Communication on the Third Polish-Soviet Colloquium on Phosphorus Chemistry, Łódź, 24–26 September, 1980.

[7] H. E. Zaugg, W. B. Martin, *Org. React.* **14**, 52 (1965).