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SYNTHESIS OF NEW ORGANOPHOSPHORUS DERIVATIVES OF ACYLUREAS AND ACYLSEMICARBAZIDES

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Abstract : A convenient route to phosphorus acylureas and acylsemicarbazides is reported. The syntheses of the new compounds involve the reaction between a chloroacetyl compound and various phosphorus starting materials (dithiophosphate, phosphine, phosphite and phosphinite).

As part of our interest in the emergence of new chemicals in the field of agropharmaceutical manufacturing[1], we have been interested in the synthesis of a series of structurally related compounds belonging to the two following families : phosphorus acylureas and phosphorus acylsemicarbazides.

Indeed, numerous acylureas[2], and particularly benzoylphenylureas such as diflubenzuron (Scheme 1), are known as insect growth regulators. The use of acylsemicarbazides of the general formula RC(O)NHC(O)NHNHR' is also described in the literature[3]. In addition, the phosphorus function introduced in our

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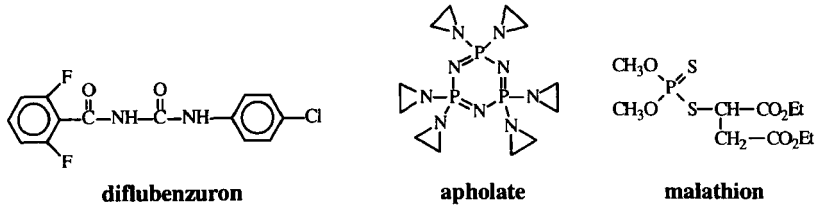
target molecules, could serve both as a carrier, as in the case of the phosphazenic derivative apholate, or as an active part of the molecule, like the dithiophosphate function in malathion (Scheme 1).

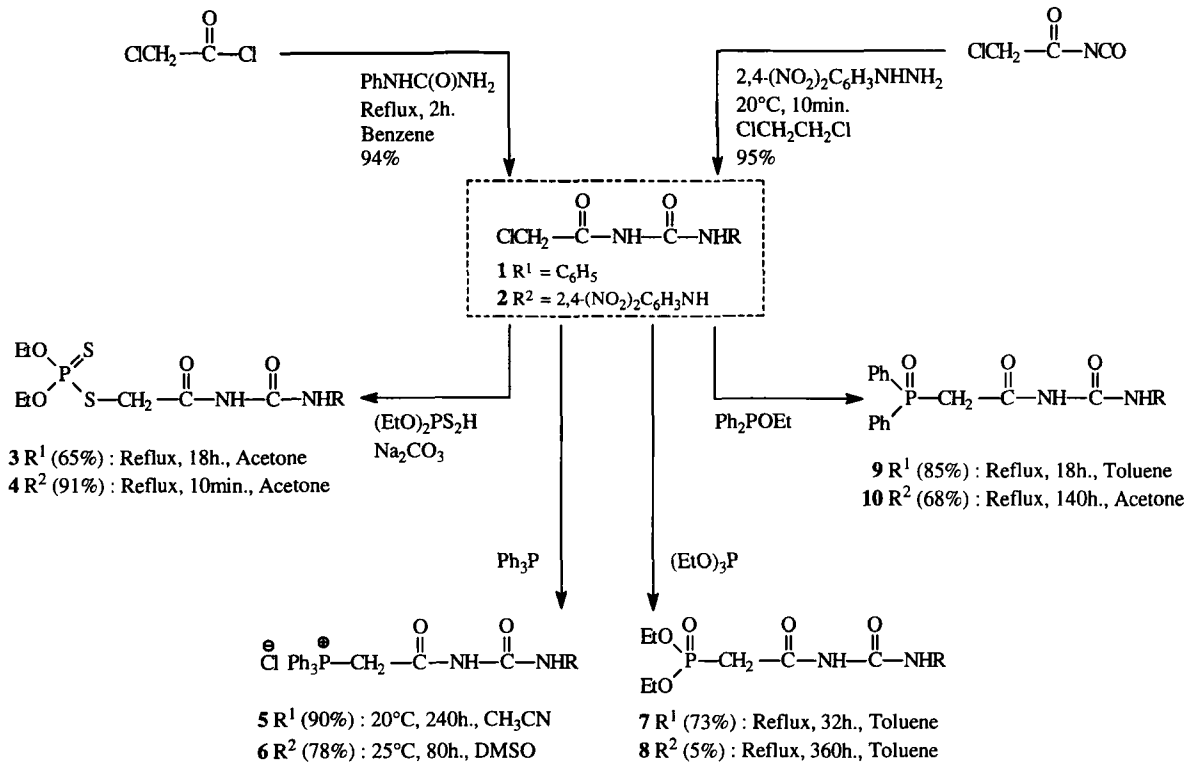


diflubenzuron **apholate** **malathion**

Scheme 1

In order to obtain the target molecules, we first synthesized two chlorinated precursors, one for each family of compounds : N-chloroacetyl-N'-phenylurea **1** and 4-chloroacetyl-1-(2',4'-dinitrophenyl)semicarbazide **2**. The urea derivative **1** was prepared from chloroacetylchloride and phenylurea (Scheme 2), according to the procedure reported in the literature[4]; however, the yield was optimized (from 70 to 94%). A different strategy was used to prepare the intermediate compound **2**: as the various acylsemicarbazides described in the literature were usually obtained by condensation between the corresponding acylisocyanates and hydrazines[5], the new acylsemicarbazide **2** was prepared easily and nearly quantitatively (95%) using chloroacetylisocyanate and 2,4-dinitrophenylhydrazine as starting materials.

The reactions of these two precursors with the sodium O,O-diethyl dithiophosphate, formed *in situ,* were realized under similar conditions (reflux in acetone) and gave the expected products **3** and **4**. In the case of the phosphorus



Scheme 2

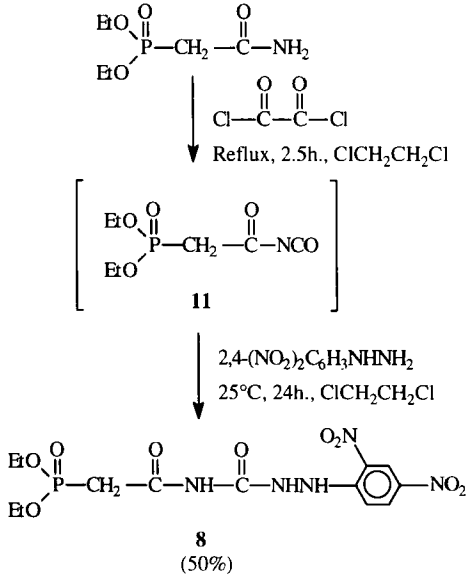
acylurea **3**, already known for its anticholinesterase activity, the yield was slightly improved (65 *versus* 55%) in comparison with the reaction given in the literature[6]. It should be noticed that, in contrast with the synthesis of **3**, the condensation involving the precursor **2** was complete very quickly (10 minutes) and the original compound **4** was obtained in a very good yield (91%). In this case, however, an increase of the heating time caused a decrease in the yield (48% after 30 minutes, 0% after 60 minutes), due to the cleavage of a C(O)-N bond with formation of 2,4-dinitrophenylsemicarbazide. The acylsemicarbazide **2** is more reactive than the precursor **1**, probably owing to the stronger electron-withdrawing effect of the two nitro groups.

Quaternizations of triphenylphosphine by **1** and **2** worked well at room temperature; however, the solvent must be suited to the different solubilities of starting materials. For instance, in acetonitrile (solvent used in the synthesis of the phosphonium salt **5**), the solubility of **2** was very low, and consequently, the rate of the reaction was very slow : the expected salt **6** was formed in only 44% yield after 15 days at room temperature. However, the use of a solvent like dimethylsulfoxide, in which the precursor **2** is completely soluble, allowed the reaction time to be reduced, and after 3 days, the phosphonium salt **6** could be isolated in a good yield (78%). The use of higher temperatures was prohibited because of the instability of the chlorides **5** and **6** under such conditions. For example, when the condensation between **1** and triphenylphosphine was conducted under reflux in acetonitrile, complete decomposition of **5** took place to afford methyl-triphenylphosphonium chloride and phenylurea, while the same reaction at room

temperature allowed us to isolate the expected salt **5** in an excellent yield (90%). The instability of this salt towards heating was proved by decomposition tests using pure product **5** as a starting material. Apparently, the nature of the counter-anion influences significantly the stability of the phosphonium moiety : **5** is much more labile than the corresponding bromide, which can be prepared at 110°C (reflux in dioxane) from N-bromoacetyl-N'-phenylurea and triphenylphosphine in a 70% yield[7].

The Michaelis-Arbuzov reaction between **1** and triethylphosphite gave the expected phosphonate **7** in a better yield (69% from the starting materials) than the synthesis involving a phosphonoacetylisocyanate (32%)[8]. In contrast, the condensation between triethylphosphite and **2** proceeded very slowly and afforded the Michaelis-Arbuzov product **8** in a very poor yield : only 23% of starting material **2** was reacted after 15 days in refluxing toluene affording 5% of **8**. Even in a solvent like acetone, in which **2** is a little more soluble, the reaction gave only 2% yield. In dimethylsulfoxide, the expected compound was not formed at all. In order to obtain the phosphonate **8** in a suitable yield, the sodium diethylphosphite was used as a more reactive nucleophilic phosphorus agent. But the Michaelis-Becker reaction from **2** did not afford the expected product. For this reason, in this case, another strategy has been used in which the carbazide function was formed during the last step of the synthesis by condensation between the phosphorus acylisocyanate **11** and 2,4-dinitrophenylhydrazine (Scheme 3). In this way, **8** can be isolated in a better yield (50% instead of 5% for the Michaelis-Arbuzov reaction) under mild conditions. This product, like the corresponding dithiophosphate **4** and

phosphonium salt **6**, showed some instability in the reaction conditions, even at room temperature (when the reaction time was modified from 24 to 80 hours, the yield decreased from 50 to 39%). However, these compounds are very stable towards heating when they are isolated.



Scheme 3

The Michaelis-Arbuzov reactions between the two precursors and ethyl diphenylphosphinite allowed us to isolate the expected phosphine oxides **9** and **10** in better yields (respectively 85 and 68%) than the reaction involving triethylphosphite. This is certainly due to the higher nucleophilicity of phosphinite in comparison with phosphite. Because of the very weak solubility of **10** in most of the common organic solvent (except dimethylsulfoxide), it was not possible to find a suitable solvent for recrystallization. For this reason, the experimental

percentages of elemental analysis of **10** were only near to theoretical values, even if NMR spectra (^{1}H, ^{13}C and ^{31}P) did not show any parasitic signals.

Conclusion

All the expected phosphorus acylureas and acylsemicarbazides can be prepared by reaction between a common precursor (**1** or **2**) and the various phosphorus starting materials. These compounds will be submitted to agrochemical tests.

Experimental

Mass spectra were recorded on a JEOL JMS-DX 300 spectrometer with ionizing energy of 70eV. ^{1}H (200 MHz), ^{13}C (50.3 MHz) and ^{31}P (80.1 MHz) NMR spectra were taken on a BRUKER Ac 200 with tetramethylsilane or phosphoric acid (85%) as reference (the chemical shift values are given in ppm and the coupling constants are measured in Hertz). IR spectra were recorded on a PERKIN-ELMER 377. Melting points were determined on a METTLER FP5 apparatus.

Chloroacetylisocyanate[9] and O,O-diethyl (carbamoylmethyl)phosphonate[10] were prepared according to the procedure described in the literature. The isocyanate was used after distillation, whereas the phosphorus acetamide was purified by recrystallization.

N-Chloroacetyl-N'-phenylurea 1 : The reaction was carried out under dry nitrogen. A mixture of chloroacetylchloride (10.8 g, 96 mmol) and phenylurea (10.9 g, 80 mmol) was refluxed for 2 hours in anhydrous benzene (50 mL). After cooling, the expected urea **1** was isolated by filtration in 94% yield (16 g, 75 mmol); m.p. 163°C (lit.[4] 161-162°C); ^{1}H-NMR (acetone-d_6) δ : 4.4 (s, 2H), 7.1 (t, 1H, J = 7.2), 7.3 (~t, 2H, J ≅ 8), 7.6 (d, 2H, J = 8), 9.8 (s), 10.3 (s).

4-Chloroacetyl-1-(2',4'-dinitrophenyl)semicarbazide 2 : The reaction was carried out under dry nitrogen. 2,4-dinitrophenylhydrazine (3.4 g, 17 mmol) was added to a solution of chloroacetylisocyanate (2 g, 17 mmol) in anhydrous 1,2-dichloroethane (100 mL). After 10 mn. at 20°C, the expected semicarbazide **2** was isolated by filtration and did not need any recrystallization. The yield was 95% (5.1 g, 16.1 mmol); m.p. 240°C; C,H,N-analysis $C_9H_8ClN_5O_6$: Calcd. C, 34.03, H, 2.54, N, 22.05, Found C, 34.0, H, 2.6, N, 21.5; ^{1}H-NMR (DMSO-d_6) δ : 4.5 (s, 2H), 7.3 (d, 1H, J = 9.5), 8.4 (dd, 1H, J = 9.5 and 2.6), 8.9 (d, 1H, J = 2.6), 10.1 (s, 1H), 10.2 (s, 1H), 11.1 (s, 1H); ^{13}C-NMR (DMSO-d_6) δ : 43.3, 115.8, 123.1, 129.9, 130.2, 137.0, 148.8, 152.9, 167.9; Mass spectrum m/z (relative intensity) : 317 ([M]$^{+\cdot}$,3.5), 281 (81), 234 (26), 210 (83), 180 (31), 122 (39), 119 (16), 94 (56), 79 (100); IR (Kbr) : 625, 740, 1140, 1240, 1275, 1310, 1335, 1485, 1510, 1580, 1615, 1685, 1715, 3320 and 3350 cm^{-1}.

O,O-diethyl (phenylaminocarbamoylcarbonylmethyl)dithiophosphate 3 : A solution of N-chloroacetyl-N'-phenylurea **1** (2 g, 9.4 mmol) in acetone (20 mL)

was added to an equimolar mixture of O,O-diethyl dithiophosphate (1.75 g, 9.4 mmol) and sodium carbonate (1 g, 9.4 mmol). After 18 hours reflux, the sodium chloride and sodium hydrogenocarbonate formed during the reaction were filtered off. The dithiophosphate **3** obtained after concentration of the filtrate was purified by column chromatography (silica gel, ether). The yield was 65% (2.2 g, 6.1 mmol); m.p. 87°C (lit.[6] 84-86°C); ^{1}H-NMR ($CDCl_3$) δ : 1.3 (t, 6H, J = 7), 3.8 (d, 2H, $^{3}J_{PH}$ = 16.5), 4.2 (m, 4H), 7.1 (t, 1H, J = 7.2), 7.35 (~t, 2H, J ≅ 8), 7.6 (d, 2H, J = 8), 9.9 (s, 1H), 10.4 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ : 15.7 (d, 8.3), 37.1 (d, 3.4), 64.6 (d, 6), 120.3, 124.6, 129.0, 136.6, 151.5, 170.1 (d, 3.8); ^{31}P-NMR ($CDCl_3$) δ : 92.3.

O,O-diethyl [1 - (2',4'- dinitrophenyl) - 4 - semicarbazidyl] carbonylmethyl] dithiophosphate 4 : 4-chloroacetyl-1-(2',4'-dinitrophenyl)semicarbazide **2** (1 g, 3.15 mmol) was added to an equimolar mixture of O,O-diethyl dithiophosphate (0.58 g, 3.15 mmol) and sodium carbonate (0.33 g, 3.15 mmol) in acetone (50 mL). After 10 mn. reflux, the sodium chloride and sodium hydrogenocarbonate formed during the reaction were filtered off. The dithiophosphate **4** obtained after concentration of the filtrate was purified by column chromatography (silica gel, ether). The yield was 91% (1.34 g, 2.9 mmol); $m.p._{(MeOH)}$ 143°C; C,H,N-analysis $C_{13}H_{18}N_5O_8PS_2$: Calcd. C, 33.4, H, 3.88, N, 14.98, Found C, 33.7, H, 4.2, N, 14.8 ; ^{1}H-NMR ($CDCl_3$) δ : 1.3 (t, 6H, J = 7), 3.8 (d, 2H, $^{3}J_{PH}$ = 21.2), 4.2 (m, 4H), 7.4 (d, 1H, J = 9.4), 8.3 (dd, 1H, J = 9.4 and 2.4), 9.1 (s, 1H), 9.15 (d, 1H, J = 2.4), 9.5 (s, 1H), 10 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ : 15.8 (d, 7.9), 36.9 (d, 3.5),

65.4 (d, 7), 114.6, 123.6, 130.4, 131.4, 139.0, 148.4, 152.5, 169.9 (d, 1.9); ^{31}P-NMR ($CDCl_3$) δ : 93.7; Mass spectrum m/z (relative intensity) : 467 ([M]$^+$,1.2), 269 (3.2), 227 (10), 180 (32), 153 (35), 125 (58), 97 (94), 69 (100); IR (Kbr) : 665, 970, 1010, 1025, 1140, 1230, 1280, 1315, 1330, 1420, 1490, 1515, 1605, 1710, 1735, 3260 and 3380 cm^{-1}.

(Phenylaminocarbamoylcarbonylmethyl)triphenylphosphonium chloride 5 : Equimolar amounts of N-chloroacetyl-N'-phenylurea **1** (2 g, 9.5 mmol) and triphenylphosphine (2.5 g, 9.5 mmol) were stirred at 20°C for 240 hours in acetonitrile (20 mL). The expected phosphonium salt **5** was isolated by filtration in 90% yield (4.0 g, 8.5 mmol); $m.p._{(MeOH)}$ 180°C; C,H,N-analysis $C_{27}H_{24}ClN_2O_2P$: Calcd. C, 68.28, H, 5.09, N, 5.90, Found C, 68.3, H, 5.0, N, 6.0; ^{1}H-NMR ($CDCl_3$) δ : 5.6 (d, 2H, $^2J_{PH}$ = 13.7), 7 (t, 1H, J = 7.2), 7.2 (~t, 2H, J ≅ 8), 7.4 (d, 2H, J = 8), 7.5-8 (m, 15H), 9.6 (s, 1H), 11.7 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ : 33.5 (d, 59.5), 117.9 (d, 89.2), 119.7, 123.7, 128.6, 130.1 (d, 13.2), 133.8 (d, 10.7), 135.0 (d, 3), 137.2, 149.5, 165.3; ^{31}P-NMR ($CDCl_3$) δ : 21.9; Mass spectrum (FAB$^+$) m/z (relative intensity) : 439 ([M-Cl]$^+$,52), 346 (26), 320 (29), 303 (100), 183 (27), 91 (12), 77 (11); IR (Kbr) : 690, 715, 740, 760, 1110, 1180, 1225, 1310, 1440, 1445, 1490, 1500, 1550, 1600, 1660, 1700, 2880 and 3400 cm^{-1}.

[{1 - (2',4' - Dinitrophenyl) - 4 - semicarbazidyl} carbonylmethyl] triphenyl phosphonium chloride 6 : Equimolar amounts of 4-chloroacetyl-1-(2',4'-dinitrophenyl)semicarbazide **2** (0.57 g, 1.8 mmol) and triphenylphosphine (0.47 g, 1.8 mmol) were stirred at 25°C for 80 hours in DMSO (4 mL). The expected

phosphonium salt **6** was isolated by precipitation in ether in 78% yield (0.81 g, 1.4 mmol); m.p.$_{(MeOH / AcOEt)}$ 204°C; C,H,N-analysis $C_{27}H_{23}ClN_5O_6P$: Calcd. C, 55.92, H, 4.00, N, 12.08, Found C, 55.8, H, 4.0, N, 12.1; ^{1}H-NMR (DMSO-d_6) δ : 5.7 (d, 2H, $^2J_{PH}$ = 14), 7.2 (d, 1H, J = 9.5), 7.6-8.2 (m, 15H), 8.4 (dd, 1H, J = 9.5 and 2.5), 8.9 (d, 1H, J = 2.5), 10.1 (s, 1H), 10.15 (s, 1H), 11.7 (s, 1H); ^{13}C-NMR (DMSO-d_6) δ : 32.3 (d, 59), 115.4, 118.3 (d, 88.8), 122.9, 129.9, 130.1, 130.2 (d, 12.8), 133.8 (d, 10.2), 134.9 (d, 2.2), 136.9, 148.5, 152.2, 165.3; ^{31}P-NMR (DMSO-d_6) δ : 21.4; Mass spectrum (FAB$^+$) m/z (relative intensity) : 544 ([M-Cl]$^+$,56), 346 (74), 303 (92), 277 (53), 183 (42), 90 (33), 77 (59); IR (Kbr) : 690, 740, 760, 1110, 1190, 1250, 1280, 1310, 1335, 1430, 1510, 1580, 1615, 1685, 1740 and 3260 cm^{-1}.

O,O-diethyl (phenylaminocarbamoylcarbonylmethyl)phosphonate 7 : An equimolar mixture of N-chloroacetyl-N'-phenylurea **1** (3 g, 14 mmol) and triethylphosphite (3.7 g, 14 mmol) was refluxed for 32 hours in toluene (50 mL). After removal of the solvent, the phosphonate **7** was purified by column chromatography (silica gel, ether). The yield was 73% (3.2 g, 10.2 mmol); m.p. 90°C (lit.[8] 91-93°C); ^{1}H-NMR ($CDCl_3$) δ : 1.3 (t, 6H, J = 7), 3.1 (d, 2H, $^2J_{PH}$ = 22), 4.2 (m, 4H), 7.1 (t, 1H, J = 7.2), 7.2 (~t, 2H, J ≅ 8), 7.5 (d, 2H, J = 8), 10.2 (s, 1H), 10.4 (s, 1H); ^{31}P-NMR ($CDCl_3$) δ : 20.2.

O,O-diethyl [1 - (2',4' - dinitrophenyl) - 4 - semicarbazidyl] carbonylmethyl] phosphonate 8 :

a) Michaelis-Arbuzov reaction : An equimolar mixture of 4-chloroacetyl-1-(2',4'-

dinitrophenyl)semicarbazide **2** (1.5 g, 4.7 mmol) and triethylphosphite (0.78 g, 4.7 mmol) was refluxed for 360 hours in toluene (50 mL). The unreacted carbazide was isolated by filtration (1.15 g, 77%). The phosphonate **8** obtained after concentration of the filtrate was purified by column chromatography (silica gel, ethyl acetate). The yield was 5% (0.10 g, 0.24 mmol); $m.p._{\cdot(AcOEt)}$ 172°C; C,H,N-analysis $C_{13}H_{18}N_5O_9P$: Calcd. C, 37.24, H, 4.33, N, 16.70, Found C, 37.2, H, 4.1, N, 16.4; ^{1}H-NMR ($CDCl_3$) δ : 1.4 (t, 6H, J = 7), 3.2 (d, 2H, $^2J_{PH}$ = 22.5), 4.2 (m, 4H), 7.3 (d, 1H, J = 9.5), 8.2 (dd, 1H, J = 9.5, J = 2.5), 9.1 (d, 1H, J = 2.5), 9.5 (s, 1H), 10 (s, 1H), 10.5 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ : 16.2 (d, 6.1), 36.4 (d, 129.4), 63.6 (d, 6.7), 114.8, 123.2, 130.0, 130.8, 138.4, 148.3, 153.4, 166.8 (d, 5.1); ^{31}P-NMR ($CDCl_3$) δ : 20.3; Mass spectrum m/z (relative intensity) : 419 ($[M]^{+\cdot}$,1.5), 346 (2.6), 267 (1.3), 179 (68), 151 (94), 123 (100), 109 (45), 79 (40); IR (Kbr) : 740, 830, 975, 1030, 1045, 1220, 1275, 1310, 1340, 1500, 1590, 1620, 1695, 1730, 2980 and 3360 cm^{-1}.

b) From the phosphonomethylisocyanate **11** : The reaction was carried out under dry nitrogen. Oxalylchloride (1.05 g, 8.2 mmol) was added to a solution of O,O-diethyl (carbamoylmethyl)phosphonate (1.15 g, 5.9 mmol) in anhydrous 1,2-dichloroethane (10 mL). The mixture was refluxed for 2.5 hours. After removal of the solvent , an equimolar amount of 2,4-dinitrophenylhydrazine (1.17 g, 5.9 mmol) and anhydrous 1,2-dichloroethane (10 mL) were added to the isocyanate **11**, obtained as a thick oil, and the mixture was stirred at 25°C for 24 hours. The expected acylsemicarbazide **8** was isolated by chromatography (silica gel, ethyl acetate). The yield was 50% (1.24 g, 3 mmol); m.p. 172°C.

Diphenyl(phenylaminocarbamoylcarbonylmethyl)phosphine oxide 9 : The reaction was carried out under dry nitrogen. Equimolar amounts of N-chloroacetyl-N'-phenylurea **1** (2 g, 9.5 mmol) and ethyl diphenylphosphinite (2.3 g, 9.5 mmol) were refluxed for 18 hours in anhydrous toluene (50 mL). After cooling, the expected phosphine oxide **9** was isolated by filtration in 85% yield (3.1 g, 8.1 mmol); $m.p._{(Benzene)}$ 207°C; C,H,N-analysis $C_{21}H_{19}N_2O_3P$: Calcd. C, 66.65, H, 5.06, N, 7.41, Found C, 67.1, H, 5.2, N, 7.5; ^{1}H-NMR ($CDCl_3$) δ : 3.6 (d, 2H, $^2J_{PH}$ = 13.6), 6.9-8.1 (m, 15H), 10.1 (s, 1H), 10.4 (s, 1H); ^{13}C-NMR ($CDCl_3$) δ : 40.2 (d, 58.6), 120.3, 124.0, 128.7, 128.9 (d, 12.5), 130.6 (d, 104.7), 130.8 (d, 10.1), 132.6 (d, 2.8), 137.0, 150.32, 167.2 (d, 5.3); ^{31}P-NMR ($CDCl_3$) δ : 26.4; Mass spectrum m/z (relative intensity) : 378 ($[M]^{+\cdot}$,2), 335 (9), 286 (18), 243 (10), 215 (72), 201 (100), 119 (20), 93 (84), 77 (24); IR (Kbr) : 685, 700, 745, 1125, 1170, 1210, 1280, 1435, 1440, 1490, 1550, 1600, 1690, 1710, 3140 and 3250 cm^{-1}.

Diphenyl [{1 - (2',4' - dinitrophenyl) - 4 - semicarbazidyl} carbonylmethyl] phosphine oxide 10 : The reaction was carried out under dry nitrogen. Equimolar amounts of 4-chloroacetyl-1-(2',4'-dinitrophenyl)semicarbazide **2** (1 g, 3.15 mmol) and ethyl diphenylphosphinite (0.77 g, 3.15 mmol) were refluxed for 140 hours in anhydrous acetone (30 mL). After cooling, the phosphine oxide **10** was isolated by filtration in 68% yield (1.03 g, 2.15 mmol); m.p. 224°C; C,H,N-analysis $C_{21}H_{18}N_5O_7P$: Calcd. C, 52.18, H, 3.75, N, 14.49, Found C, 50.7, H, 4.0, N, 13.6; ^{1}H-NMR (DMSO-d_6) δ : 4 (d, 2H, $^2J_{PH}$ = 14.1), 7.2 (d, 1H, J = 9.6), 7.8 (m, 10H),

8.4 (dd, 1H, J = 9.6, J = 2.5), 8.9 (d, 1H, J = 2.5), 10.1 (s, 1H), 10.2 (s, 1H), 11 (s, 1H); ^{13}C-NMR (DMSO-d_6) δ* : 115.7, 123.2, 128.8 (d, 12), 129.8, 130.2, 130.5 (d, 9.7), 132.2 (d, 2.7), 133.1 (d, 102), 136.9, 148.8, 152.91, 167.2 (d, 6); ^{31}P-NMR (DMSO-d_6) δ : 26.4; Mass spectrum (FAB$^+$) m/z (relative intensity) : 484 ([M+H]$^+$,4); IR (Kbr) : 690, 800, 820, 1020, 1125, 1170, 1280, 1330, 1440, 1505, 1590, 1610, 1685, 1735, 2980, 3280 and 3330 cm^{-1}.

*The CH_2P is hidden by the signal of DMSO-d_6 (38 to 41 ppm)

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