Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2009, **19**, 263–265

Mendeleev Communications

Effect of anomalous aryl strengthening in the series of *N*-phosphorylureas

Alfiya M. Safiulina,[a] Evgenii I. Goryunov,*[b] Aleksandr A. Letyushov,[a] Irina B. Goryunova,[b] Sof'ya A. Smirnova,[b] Allan G. Ginzburg,[b] Ivan G. Tananaev,[a] Edward E. Nifant'ev[b] and Boris F. Myasoedov[a]

[a] *A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 955 4641; e-mail: alfiya_safiulina@mail.ru*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5085; e-mail: phoc@ineos.ac.ru*

DOI: 10.1016/j.mencom.2009.09.010

Within the series of model *N*-diorganophosphoryl-*N'*-*n*-octylureas, the ability to extract uranium(VI) from nitric acid solutions is maximal for *N*-diphenylphosphoryl derivative and sharply decreases when phenyl groups are replaced with *n*-alkyl or cycloalkyl substituents; this indicates the presence of 'anomalous aryl strengthening' effect also in the series of *N*-phosphorylureas, a new promising class of organophosphorus extractants.

A so-called 'anomalous aryl strengthening' (AAS) effect was revealed in the study of structure dependence of extractive power for a number of bidentate neutral organophosphorus compounds (BNOPC).[1] This effect consists in the substantial growth of the extractive power of BNOPC when alkyl substituents at phosphorus atom are replaced with aryl groups, even though it is accompanied by a simultaneous decrease in the basicity of these compounds. This phenomenon was discovered for a series of P,P,P′,P′-tetrasubstituted methylenediphosphine dioxides[2] and later was revealed for carbamoylmethylphosphine oxides.[3] At present, there is no uniform opinion on the origin of AAS effect;† however, its significance for purposeful search for new high-throughput extractants within BNOPC series can scarcely be exaggerated. Thus, in particular, the most practically important carbamoylmethylphosphine oxide extractants were revealed just among compounds containing diphenylphosphoryl fragments.[5,6]

It is necessary to emphasize, however, that the AAS effect was observed until now only for two structurally related types of BNOPC whose molecules contain liganding groups (phosphoryl or phosphoryl and carbonyl) connected by identical methylene bridge, *i.e.*, the existence of this effect for BNOPC with linkers of another nature remained unclear.

Moreover, the elucidation of this issue is crucial to solve a number of important problems to optimize the search for the most efficient extractants among entirely new types of BNOPC, in particular, to reveal the nature of factors that determine unusually high extractive power of *N*-diphenylphosphoryl-*N'*-*n*-alkyl(C_6–C_{10})ureas $Ph_2P(O)NHC(O)NHC_nH_{2n+1}$ **1** (n = 6–10) toward 4*f* and 5*f* elements.[7]

For this purpose, we have prepared a number of model *N*-diorganophosphoryl-*N'*-*n*-octylureas RR′P(O)NHC(O)NH-(n-C_8H_{17}) **2** (R = Me, R′ = Ph), **3** (R = R′ = n-C_6H_{13}) and **4** (R = R′ = *cyclo*-C_6H_{11}), whose molecules contain hydrocarbon residues of different nature bound to the phosphorus atom *via* P–C bonds and identical *n*-octyl substituent at the terminal nitrogen atom, and studied their extractive properties toward uranium(VI).

This set of model compounds made it possible to compare most correctly their extractive characteristics with those of *N*-diphenylphosphoryl-*N'*-*n*-octylurea **1a** (n = 8), the best extractant among the compounds of type **1**, and to reveal the presence or absence of AAS effect within the series of N-phosphorylated ureas.

To obtain all these compounds, we used a potentially simplest, efficient and industrially feasible approach to the synthesis of N-phosphorylated ureas, which was elaborated previously for preparing various *N*-diphenylphosphorylureas,[8] including ureas of type **1**.[9] This approach consists in the use of one-pot processes involving as many stages as possible, the key stage is the transformation of phosphoryl chlorides into corresponding phosphoryl isocyanates in the presence of a weak Lewis acid, anhydrous magnesium chloride, as an electrophilic catalyst.[10]

N-Methyl(phenyl)phosphoryl-*N'*-*n*-octylurea **2** was obtained starting from commercially available methyl(phenyl)phosphoryl chloride with the use of two-stage one-pot process (Scheme 1).

$$\mathrm{PhMeP(O)Cl} \xrightarrow[\sim 20\ ^\circ\mathrm{C},\ \mathrm{MeCN}]{\mathrm{NaOCN},\ [\mathrm{MgCl_2}]} \underset{\mathbf{5}}{[\mathrm{PhMeP(O)NCO}]} \xrightarrow[\sim 20\ ^\circ\mathrm{C}]{n\text{-}\mathrm{C_8H_{17}NH_2}} \underset{\mathbf{2}}{\mathrm{PhMeP(O)NHC(O)NH}(n\text{-}\mathrm{C_8H_{17}})}$$

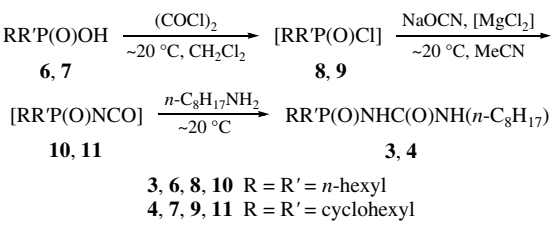
Scheme 1

The first stage of this process is the reaction of the chlorophosphinate with sodium cyanate in the presence of 2.5 mol% $MgCl_2$ in anhydrous acetonitrile medium. The reaction is complete within 1 h at ambient temperature, while the yield of methyl(phenyl)phosphoryl isocyanate **5** is 93% according to $^{31}P\{^1H\}$ NMR spectra. The resultant isocyanate as acetonitrile solution was further reacted with *n*-octylamine to give urea **2** in 88% yield.

Phosphorylureas **3** and **4** were also obtained *via* one-pot processes (three-stage in this case) using di-*n*-hexylphosphinic (**6**) and dicyclohexylphosphinic (**7**) acids, respectively, as starting compounds (Scheme 2).

These acids were treated with oxalyl chloride in methylene chloride to form di-*n*-hexylphosphinic (**8**) and dicyclohexyl-

† It is the most widespread opinion that this effect is related to the amphoteric nature of aryl substituents showing both donor and acceptor properties depending on certain factors such as reaction center nature, attacking reagent character, solvent nature, *etc*.[4]



Scheme 2

phosphinic (**9**) chlorides in 98 and ~100% yields, respectively (according to $^{31}P\{^1H\}$ NMR spectra), which were further reacted (without additional purification) with sodium cyanate to produce di-*n*-hexylphosphoryl (**10**) and dicyclohexylphosphoryl (**11**) isocyanates. The reaction of these isocyanates with *n*-octylamine leads to phosphorylureas **3** and **4** in 83 and 72% yields, respectively.

Note that the developed one-pot processes do not require the isolation of intermediate hydrolytically unstable compounds (phosphoryl chlorides **8**, **9** and phosphoryl isocyanates **5**, **10** and **11**) in an individual state, all process stages proceed at ambient temperature, and target ureas **2**–**4** are obtained in rather high yields and in high purity. The structure of the ureas was confirmed by elemental analysis data, IR and ^1H and $^{31}P\{^1H\}$ NMR spectra.‡

The study of the ability of *N*-diorganophosphorylureas **1a** and **2**–**4** to extract U^{VI} from nitric acid solutions showed that the replacement of one (urea **2**) or two phenyl groups (urea **3**) with normal alkyl fragment results in a substantial (almost threefold) decrease in extractive power as compared with reference N-diphenylphosphorylated urea **1a**. For urea **4**, where both phenyl fragments are replaced with their fully hydrogenated analogues, cyclohexyl substituents, the extractive power decreases by almost 40 times (Figure 1).

Taking into account that ureas **1a** and **2**–**4** have identical terminal nitrogen-containing fragments and differ only in the nature of organic substituents connected to the phosphorus atom *via* C–P bonds, it is safe to associate the high extractive power of N-diphenylphosphorylated ureas of type **1** toward uranium(VI) with the AAS effect.

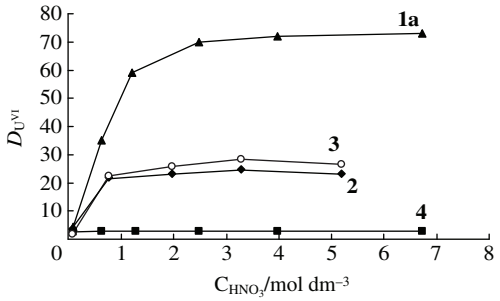


Figure 1 Extraction of U^{VI} with 0.05 mol dm^{-3} solutions of *N*-diorganophosphoryl-*N*′-*n*-octylureas **1a**, **2**–**4** in chloroform depending on HNO_3 concentration (phase ratio of 1:1).

Thus, on the basis of our experimental data, we can draw a conclusion that the 'anomalous aryl strengthening' effect is observed not only for methylenediphosphine dioxides and carbamoylmethylphosphine oxides but also for *N*-diorganophosphorylureas; that is, this effect has a rather general character in the series of bidentate neutral organophosphorus compounds.

This work was supported by the Russian Foundation for Basic Research (project nos. 05-03-08017-ofi_e and 08-03-12153-ofi)

‡ The NMR spectra were recorded on a Bruker AV-400 spectrometer operating at 400.13 (^1H) and 161.98 MHz (^{31}P) in $CDCl_3$ solutions using the signals of residual protons of the deuterated solvent as an internal reference for ^1H NMR and 85% H_3PO_4 as an external reference for ^{31}P NMR. The IR spectra were obtained on a UR-20 spectrometer as KBr pellets. Di-*n*-hexylphosphinic acid **6** and dicyclohexylphosphinic acid **7** were obtained according to literature procedures.[11,12]

N-*Methyl(phenyl)phosphoryl*-N′-n-*octylurea* **2**. Finely divided anhydrous $MgCl_2$ (14 mg, 0.147 mmol) was added to a solution of 1.015 g (5.7 mmol) of chlorophosphinate **4** in 10 ml of anhydrous MeCN, the mixture was stirred until complete dissolution of $MgCl_2$, 0.74 g (11.4 mmol) of NaOCN was added, and the suspension was stirred for additional 1 h at ambient temperature. *n*-Octylamine (0.738 g, 5.7 mmol) was added dropwise to the resultant reaction mixture containing phosphoryl isocyanate **5** (δ $^{31}P\{^1H\}$ 26.65 ppm) and the suspension was stirred for 1 h, MeCN was removed in a vacuum, 20 ml of distilled water was added to the residue, and the mixture was stirred for 1 h. The precipitate was collected by filtration, washed with distilled water (4×20 ml), and dried in air to give 1.55 g (88%) of compound **2** as a white crystalline solid, mp 149–151 °C (from chloroform–hexane). $^{31}P\{^1H\}$ NMR, δ: 33.68. ^1H NMR, δ: 0.85 [t, 3H, *Me*$(CH_2)_7$, $^3J_{HH}$ 6.7 Hz], 1.10–1.33 [m, 10H, Me(C*H*$_2)_5$], 1.34–1.50 (m, 2H, C*H*$_2$CH$_2$NH), 1.91 (d, 3H, MeP, $^2J_{HP}$ 14.7 Hz), 3.10 (dt, 2H, C*H*$_2$NH, $^3J_{CHH}$ 6.5 Hz, $^3J_{NHH}$ 6.4 Hz), 6.35 (br. s, 1H, CH$_2$N*H*), 7.35–7.48 (m, 2H, *m*-Ph), 7.52 (t, 1H, *p*-Ph, $^3J_{HH}$ 7.1 Hz), 7.78 (dd, 2H, *o*-Ph, $^3J_{HH}$ 7.7 Hz, $^3J_{HP}$ 12.7 Hz), 8.44 [d, 1H, NHP(O), $^2J_{HP}$ 7.5 Hz]. IR (KBr, ν/cm^{-1}): 3330, 3150, 3100 (NH), 1700, 1680 (C=O), 1180 (P=O). Found (%): C, 61.94; H, 8.75; N, 9.08; P, 9.92. Calc. for $C_{16}H_{27}N_2O_2P$ (%): C, 61.92; H, 8.77; N, 9.02; P, 9.99.

N-*Di*-n-*hexylphosphoryl*-N′-n-*octylurea* **3**. Freshly distilled oxalyl chloride (0.9 g, 7.1 mmol) was added dropwise over 25 min to a magnetically stirred solution of 1.090 g (4.7 mmol) of phosphinic acid **6** in 10 ml of anhydrous CH_2Cl_2 in an argon atmosphere at ambient temperature, the mixture was stirred for additional 1.5 h at the same temperature, volatile products were removed in a vacuum from the reaction mixture containing chlorophosphinate **8** (δ $^{31}P\{^1H\}$ 73.46 ppm). The residue was dissolved in 10 ml of anhydrous MeCN, 11 mg (0.115 mmol) of finely divided anhydrous $MgCl_2$ was added to the solution, the mixture was stirred until complete dissolution of $MgCl_2$, 0.61 g (9.4 mmol) of NaOCN was added, and the suspension was stirred for 11.5 h at ambient temperature. *n*-Octylamine (607 mg, 4.7 mmol) was added dropwise to the resultant reaction mixture containing phosphoryl isocyanate **10** (δ $^{31}P\{^1H\}$ 44.10 ppm), the mixture was stirred for 1 h at ambient temperature, 17 ml of distilled water was added, and the mixture was stirred for 1 h at ambient temperature. The precipitate was collected by filtration, washed with distilled water (4×12 ml), and dried in air to give 1.50 g (83%) of compound **3** as a white crystalline solid, mp 98–99 °C (from heptane). $^{31}P\{^1H\}$ NMR, δ: 52.74. ^1H NMR, δ: 0.86 (t, 9H, Me, $^3J_{HH}$ 6.7 Hz), 1.10–1.69 [m, 28H, Me(C*H*$_2)_6$ + Me(C*H*$_2)_4$], 1.72–2.13 (m, 4H, CH$_2$P), 3.12 (dt, 2H, C*H*$_2$NH, $^3J_{CHH}$ 6.7 Hz, $^3J_{NHH}$ 6.2 Hz), 6.03 (br. s, 1H, CH$_2$N*H*), 7.94 [br. s, 1H, NHP(O)]. IR (KBr, ν/cm^{-1}): 3320, 3160, 3100 (NH), 1710, 1700, 1680 (C=O), 1165 (P=O). Found (%): C, 64.76; H, 11.63; N, 7.07; P, 8.01. Calc. for $C_{21}H_{45}N_2O_2P$ (%): C, 64.91; H, 11.67; N, 7.21; P, 7.97.

N-*Dicyclohexylphosphoryl*-N′-n-*octylurea* **4**. Freshly distilled oxalyl chloride (0.9 g, 7.1 mmol) was added dropwise over 25 min to a magnetically stirred solution of 1.090 g (4.7 mmol) of phosphinic acid **7** in 10 ml of anhydrous CH_2Cl_2 in argon atmosphere at ambient temperature, the mixture was stirred for additional 1.5 h at the same temperature, volatile products were removed in a vacuum from the reaction mixture containing chlorophosphinate **9** (δ $^{31}P\{^1H\}$ 82.22 ppm). The residue was dissolved in 10 ml of anhydrous MeCN, 11 mg (0.115 mmol) of finely divided anhydrous $MgCl_2$ was added to the solution, the mixture was stirred until complete dissolution of $MgCl_2$, 0.61 g (9.4 mmol) of NaOCN was added, and the suspension was stirred for 17.5 h at ambient temperature. *n*-Octylamine (607 mg, 4.7 mmol) was added dropwise to the resultant reaction mixture containing phosphoryl isocyanate **11** (δ $^{31}P\{^1H\}$ 49.46 ppm), and the mixture was stirred for 1 h at ambient temperature. The subsequent treatment as in the synthesis of compound **3** afforded 1.30 g (72%) of compound **4** as a white crystalline solid, mp 139–141 °C (from chloroform–hexane). $^{31}P\{^1H\}$ NMR, δ: 52.25. ^1H NMR, δ: 0.86 (t, 3H, Me, $^3J_{HH}$ 6.8 Hz), 1.13–1.53 [m, 22H, Me(C*H*$_2)_6$ + cyclo-C_6H_{11}], 1.60–2.03 (m, 12H, *cyclo*-C_6H_{11}), 3.15 (dt, 2H, C*H*$_2$NH, $^3J_{CHH}$ 6.8 Hz, $^3J_{NHH}$ 6.0 Hz), 6.50 (br. s, 1H, CH$_2$N*H*), 6.96 [br. s, 1H, NHP(O)]. IR (KBr, ν/cm^{-1}): 3320, 3080 (NH), 1700 (C=O), 1210, 1180 (P=O). Found (%): C, 65.57; H, 10.79; N, 7.41; P, 7.92. Calc. for $C_{21}H_{41}N_2O_2P$ (%): C, 65.59; H, 10.75; N, 7.28; P, 8.05.

and the Russian Academy of Sciences (programme no. 18 of Basic Research of the Presidium of the RAS 'Development of Methods for Preparing Chemical Compounds and Design of New Materials', subprogram 'Development of Methodology for Organic Synthesis and Design of Compounds with Valuable Properties of Practical Interest', project 'Development of Methods for Synthesis and Studying the Properties of New Mono- and Polydentate Organophosphorus Compounds for Radioactive Waste Partitioning').

References

1 A. M. Rozen and B. V. Krupnov, *Usp. Khim*., 1996, **65**, 1052 (*Russ. Chem. Rev*., 1996, **65**, 973).
2 A. M. Rozen, Z. I. Nikolotova, N. A. Kartashova and K. S. Yudina, *Dokl. Akad. Nauk SSSR*, 1975, **222**, 1151 (in Russian).
3 M. K. Chmutova, N. P. Nesterova, N. E. Kochetkova, O. E. Koiro and B. F. Myasoedov, *Radiokhimiya*, 1982, **24**, 31 [*Sov. Radiochem*. (*Engl. Transl.*), 1982, **24**, 27].
4 M. I. Kabachnik, B. F. Myasoedov, T. A. Mastryukova, Yu. M. Polikarpov, M. K. Chmutova and N. P. Nesterova, *Izv. Akad. Nauk, Ser. Khim*., 1996, 2624 (*Russ. Chem. Bull*., 1996, **45**, 2484).
5 B. F. Myasoedov, M. K. Chmutova, N. E. Kochetkova, O. E. Koiro, G. A. Pribylova, N. P. Nesterova, T. Ya. Medved' and M. I. Kabachnik, *Solvent Extr. Ion Exch*., 1986, **4**, 61.
6 O. I. Artyushin, E. V. Sharova, I. L. Odinets, S. V. Lenevich, V. P. Morgalyuk, I. G. Tananaev, G. A. Pribylova, G. V. Myasoedova, T. A. Mastryukova and B. F. Myasoedov, *Izv. Akad. Nauk, Ser. Khim*., 2004, 2395 (*Russ. Chem. Bull., Int. Ed*., 2004, **53**, 2499).
7 I. G. Tananaev, A. A. Letyushov, A. M. Safiulina, I. B. Goryunova, T. V. Baulina, V. P. Morgalyuk, E. I. Goryunov, L. A. Gribov, E. E. Nifant'ev and B. F. Myasoedov, *Dokl. Akad. Nauk*, 2008, **422**, 762 [*Dokl. Chem.* (*Engl. Transl.*), 2008, **422**, 260].
8 T. V. Baulina, I. B. Goryunova, P. V. Petrovskii, E. I. Matrosov, E. I. Goryunov and E. E. Nifant'ev, *Dokl. Akad. Nauk*, 2006, **409**, 486 [*Dokl. Chem*. (*Engl. Transl.*), 2006, **409**, 129].
9 E. I. Goryunov, E. E. Nifant'ev and B. F. Myasoedov, *RF Patent 2 296 768*, 2007.
10 E. I. Goryunov, G. N. Molchanova, I. B. Goryunova, T. V. Baulina, P. V. Petrovskii, V. S. Mikhailovskaya, A. G. Buyanovskaya and E. E. Nifant'ev, *Izv. Akad. Nauk, Ser. Khim*., 2005, 2543 (*Russ. Chem. Bull., Int. Ed*., 2005, **54**, 2626).
11 G. M. Kosolapov, *J. Am. Chem. Soc*., 1950, **72**, 5508.
12 B. Issleib, *Z. Anorg. Allg. Chem.*, 1954, **277**, 258.

Received: 27th February 2009; Com. 09/3291