Study on the Methyl Migration of 10-Methoxy-5, 10-dihydrophenophosphazine 10-oxide

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The title compound (1) was treated with NaH at room temperature in anhydrous DMF to give a sodium salt (containing nitrogen anion) which could shift the methyl group from oxygen to nitrogen atom to form *N*-methyl phosphinic acid as the reaction temperature was increased to 120 ℃. Three nitro derivatives containing 5,10-dihydrophenophosphazine ring system were prepared for the investigation on the above reaction mechanism which would be possibly regarded as a special inter-molecular substitution, *viz.*, the nucleophilic nitrogen anion from one molecule of 1 attacked the carbon atom of the *O*-methyl of another 1. In addition, the chemical structures of seven compounds containing 5,10-dihydrophenophosphazine ring system involved in the experiment were confirmed by IR, ^{1}H NMR, ^{31}P NMR and mass spectroscopy.

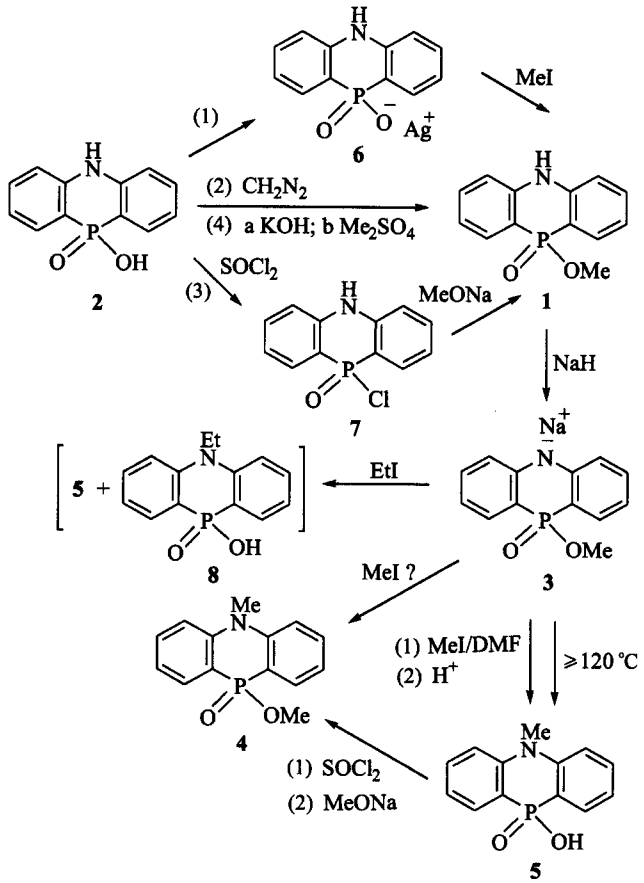
Keywords 5,10-dihydrophenophosphazine, synthesis, methyl migration, structure survey

Introduction

The compounds containing 5,10-dihydrophenophosphazine ring system can be used for determination of titanium and uranium dioxide, and also used as catalyst for the synthesis of carbodiimides and polycarbodiimides by the decarboxylation of isocyanates. And they are useful as additives for lubricating oils, greases, and hydraulic fluids used in high-temperature environments (*e.g.*, jet engines).[1] Ten years ago, Freeman and his co-workers found that the amino derivatives containing 5,10-dihydrophenophosphazine system were safe intermediates[2,3a,4] which can substitute for strong carcinogenic intermediates of β-naphthylamine and benzidine residue in some well-known carcinogenic β-naphthylamine- and benzidine-based azo dyes which are now banned.[3b,5] Obviously, it is of great importance to study the compounds containing 5,10-dihydrophenophosphazine ring system.

The title compound 10-methoxy-5,10-dihydrophenophosphazine 10-oxide (**1**) (Scheme 1) was obtained from the phosphinic acid **2** prepared by the reported method.[6] In principle, the NH group in **1** has weak acidity to some extent because of the resonance effect from the two phenyl cyclic system (Scheme 2), and can be alkylated by deprotonation with a base and treatment of the resulting anion with an alkyl halide (such as MeI, EtI, *etc.*) in nonproton polar solvent (for example, DMF). However, when the intermediate **3** obtained by the interaction of **1** and NaH reacted with MeI in DMF, the target molecule **4** was not formed at reaction temperature (≥120 ℃), but a surprising compound of 10-hydroxy-5-methyl-5,10-dihydrophenophosphazine 10-oxide (**5**, Scheme 1) was obtained, and always accompanied by a small amount of the methyl-elimination product, *i.e.*, the phosphinic acid **2**. Obviously, it is impossible to prepare the compound **4** via interaction of **3** and MeI. In fact, the compound

Scheme 1 Synthetic route to compound **1** and its relating reactions



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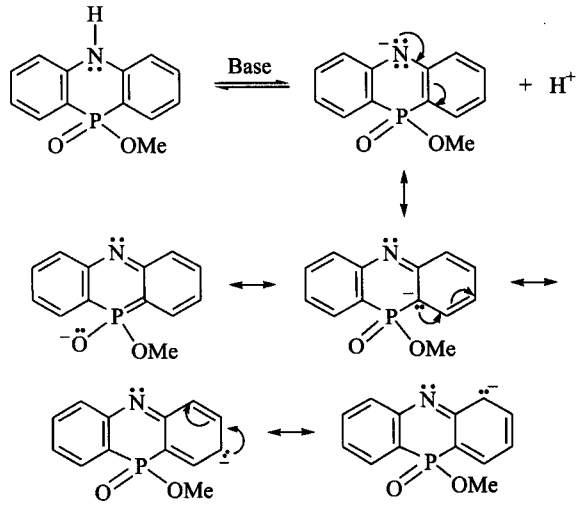
Scheme 2 Nitrogen anion obtained from **1** was stablized by the resonance effect of the two phenyl cyclic system



4 has been obtained from the compound **5** in our laboratory.

Results and discussion

Synthesis of **1**

It was reported that **1** could be obtained by four methods (Scheme 1): ① the conversion of the phosphinic acid **2** to its silver salt **6** and then allowing **6** to react with MeI;[7] ② the interaction of **2** and diazomethane;[8] ③ the conversion of **2** to its acid chloride **7** and then treatment of **7** with MeONa in MeOH;[8] ④ the conversion of the phosphinic acid **2** to its potassium salt and then allowing the potassium salt to react with Me_2SO_4.[8] However, on attempting the first method to prepare **1**, little of it was obtained. The second method came down to diazomethane which was not readily obtained and the last one involved toxic Me_2SO_4. So, **1** was prepared by the third method.

Methyl migration of **1**

When **1** was treated with NaH at room temperature followed by reacting with different moles of MeI at 120 ℃ for 2.5 h, a white solid was obtained and was characterized by HPLC mainly as the compound **5** rather than the expected compound **4**. It was once considered that **1** was firstly converted to **4** during the reaction, and followed by hydrolysis of **4** to form the compound **5**. But, the similar results reappeared even though anhydrous[9] in lieu of commercial DMF was used. What is more, there were also little distinct changes in result as the amount of MeI increased. It was therefore guessed that the *N*-methyl group in the molecule of **5** may incompletely come from MeI and partially from the *O*-methyl of **1**. In order to verify this hypothesis, the intermediate **3**, without adding any MeI, was directly heated to 120 ℃ for 2.5 h. The result revealed that the basic product was assigned by ^{1}H NMR (Fig. 1) and mass spectroscopy (Fig. 2) to be 10-hydroxy-5-methyl-5, 10-dihydrophenophosphazine 10-oxide, namely, the methyl shift product **5** (see also Entry 5 in Table 1). Obviously, **1** did shift the methyl group from oxygen to nitrogen atom under the reaction conditions.

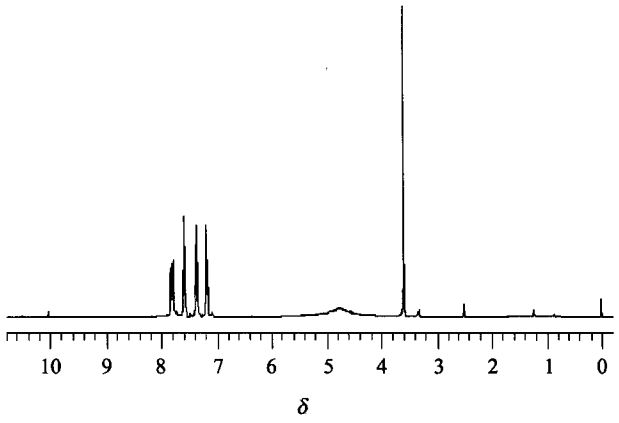


Fig. 1 ^{1}H NMR spectrum of 10-hydroxy-5-methyl-5, 10-dihydrophenophosphazine 10-oxide (**5**) (400 MHz, d^6-DMSO).

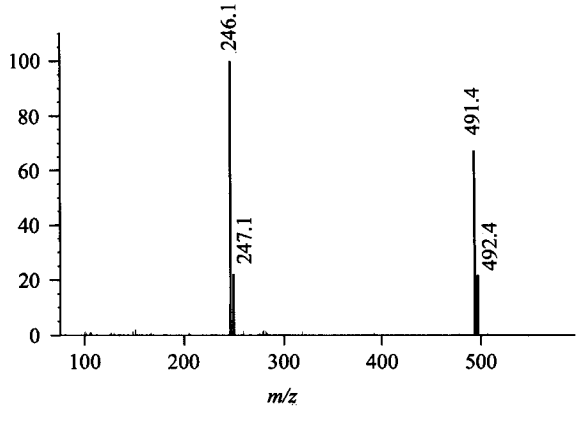


Fig. 2 Mass spectroscopy of 10-hydroxy-5-methyl-5, 10-dihydrophenophosphazine 10-oxide (**5**) (400 MHz, d^6-DMSO).

It can also be seen from Table 1 that there was always a small amount of the phosphinic acid **2** formed while **1** underwent methyl migration. The reason for this may be that the hydrogen anion (H^-), in the reaction process, could act either as a base, to attack the proton on the NH group, and make **1** become the intermediate **3**, or as a nucleophile, to attack the carbon atom of the *O*-methyl in **1** or the intermediate **3**, and make them further become two new intermediates **9** and **10** (Scheme 3) which would immediately be converted to the phosphinic acid **2** once acidified with dilute acid.

Possible mechanism of methyl group migration

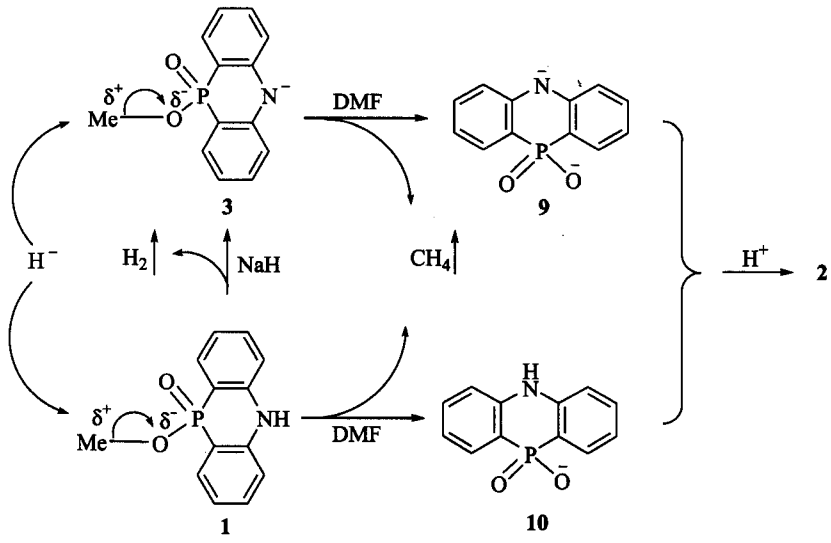
Inter-molecular reaction mechanism It was assumed from above discussion that the intermediate **3** could undergo a special inter-molecular nucleophilic substitution as in Scheme 4 to form the methyl migration product **5**.

Table 1 Influence of the amount of MeI on the *N*-methylation of **1**[a]

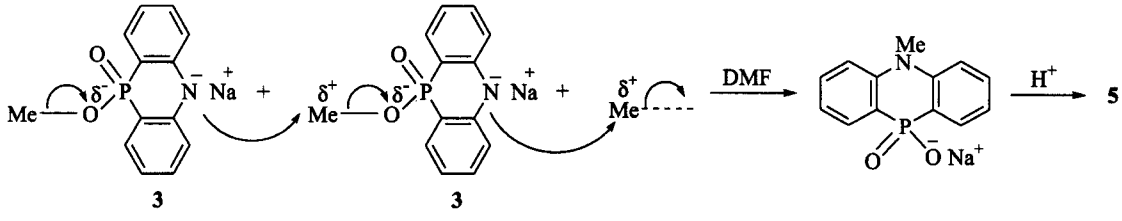
Entry	MeI (mmol)	Yield of **5**[b] (%)	Analytical results by HPLC[c] (%)		
			Product **2**	Product **5**	Reactant **1**
1	24	75.6	5.87	83.96	3.41
2	16	79.7	4.26	88.54	1.69
3	8	59.3	5.83	84.67	2.57
4	4	51.0	6.52	86.44	2.31
5	0	43.2	8.46	75.37	11.25

[a] DMF: 40 mL, **1**: 8 mmol, NaH: 8 mmol, react at 120 ℃ for 2.5 h. [b] Calculating the yield as follows: total weight of crude product times the analytical results by HPLC, and then the product divides by the weight from chemical computation. [c] Analytical conditions: chromatographic column: spherisorb C_{18}(5 μm, 250 mm × 4.6 mm), mobile phase: MeOH-H_2O (60 mL/40 mL), adding a small amount of TEBA, flow rate: 1 mL/min, detection wavelength: 285.4 nm. Note that the analytical data of impurities are not shown and all the data of HPLC in the table are abridged to two significant figures, so are those in the following Tables 2 and 3.

Scheme 3 Possible methyl-eliminating mechanism of **1** in the presence of NaH in DMF

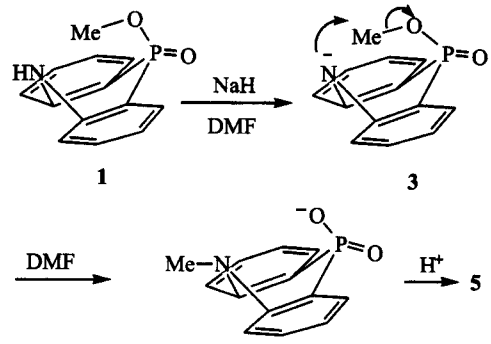


Scheme 4 Special nucleophilic substitution of the intermediate **3** in DMF



Intramolecular reaction mechanism It was reported that the heterocyclic rings of some analogues of **1**, such as 5-methyl-10-phenyl-5,10-dihydrophenophosphazine 10-oxide,[10] 5-ethyl-10-phenyl-5,10-dihydrophenophosphazine 10-sulfide,[11] 1,2-benzo-10-isopropyl-5-methyl-5,10-dihydrophenophosphazine 10-silfide,[12] *etc.*, have a boat conformation in which the noncyclic P—C bond occupies an axial position, and P = O or P = S bond occupies an equatorial position. It is therefore guessed that the heterocyclic ring of **1** has a similar boat conformation. In doing so, the intermediate **3** may also undergo intramolecolar nucleophilic substitution (S_Ni) to form product **5** (Scheme 5).

Scheme 5 Possible intramolecular nucleophilic substitution of the intermediate **3** in DMF



Verification of methyl migration mechanism

Methyl migration at different temperatures The investigation on the behavior of the intermediate **3** at different temperatures in DMF (Table 2) showed that the product **5** was obtained only at a higher temperature ($\geqslant$ 120 ℃) and was hardly obtained at or less than 60 ℃. In other words, the methyl group migration of the intermediate **3** was sensitive to the reaction temperature, which was considered to be more consistent with inter-molecular than intramolecular reaction. Because intramolecular reaction could readily carry out at a relative low temperature when the two reaction functional groups have favorable spatial location without any molecular collision with one another.

Substitution of **1** *as a nucleophilic agent* **1** (6 mmol) was treated with an equimolar amount of NaH and after hydrogen evolution ceased, to reaction system (see also Scheme 1), was added 3 mmol of EtI. The reaction system would produce two kinds of solids (white and earth-white) as was maintained at 120 ℃ for 2.5 h, therein, the basic ingredient of the white solid was the right product **5** confirmed by ^{1}H NMR (Fig. 1) and mass spectroscopy (Fig. 2), and that of the earth-white one was a different compound whose molecular weight was 259 by analysis of HP1100 High Performance Liquid Chromatography/Mass Selective Detector. After being purified, this compound was assigned by ^{1}H NMR (Fig. 3) to be 5-ethyl-10-hydroxy-5, 10-dihydrophenophosphazine 10-oxide (**8**) (Scheme 1). This result demonstrates that the intermediate **3** can act as a good nucleophile to easily attack the electrophilic center of other molecules. In other words, it could attack the *O*-methyl of another one of **3** (Scheme 4). Of course, it could also attack the *O*-methyl of itself when having favorable spatial location as shown in Scheme 5, which was so far questionable.

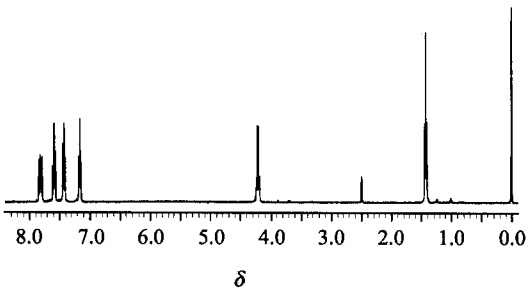


Fig. 3 ^{1}H NMR spectrum of 5-ethyl-10-hydroxy-5, 10-dihydrophenophosphazine 10-oxide (**8**) (400 MHz, d^6-DMSO).

Substitutions of **1** *and its nitro derivatives as electrophilic substrates* 10-Hydroxy-2-nitro-5, 10-dihydrophenophosphazine 10-oxide (**11**) was synthesized by nitration[7] of the phosphinic acid **2** giving the expected product **13** (Scheme 6) with a considerable content (Entry 2 in Table 3). When **11** was treated with NaH in anhydrous DMF, the resulting bis-anion **12** was allowed to react with the **1**. Noteworthily, bis-anion **12** has a deep purple-red color, which is, to be believed, due to the existence of a rapidly formed tautomeric equilibrium between the nitro and its acid form[2a,13] in the presence of NaH in DMF (Scheme 7). Although this equilibrium will weaken the nucleophilicity of **12**, it can still attack electrophilic carbon atom of *O*-methyl of **1**. In contrast to **12**, the intermediate **3** does not exhibit this tautomeric equilibrium at all, and it has almost the same stereo effect as **12** does. So its nucleophilicity should be much stronger than that of the bis-anion **12**. In so doing, the nucleophilic nitrogen anion of the intermediate **3** should more readily attack the electrophilic carbon atom of another molecule of **1**.

Table 2 Reaction results of the intermediate **3** at different temperature in DMF [a]

Entry	*T* (℃)	Yield of **5** (%)	Analytical results by HPLC[b] (%)		
			Product **2**	Product **5**	Reactant **1**
1	refluxing	50.8	5.87	84.67	2.57
2[c]	120 ± 2	43.2	8.46	75,37	11.25
3	120 ± 2	45.1	6.69	81.98	1.87
4	80 ± 2	13.5	45.83	24.59	26.57
5	60 ± 2	5.1	40.31	8.45	46.52

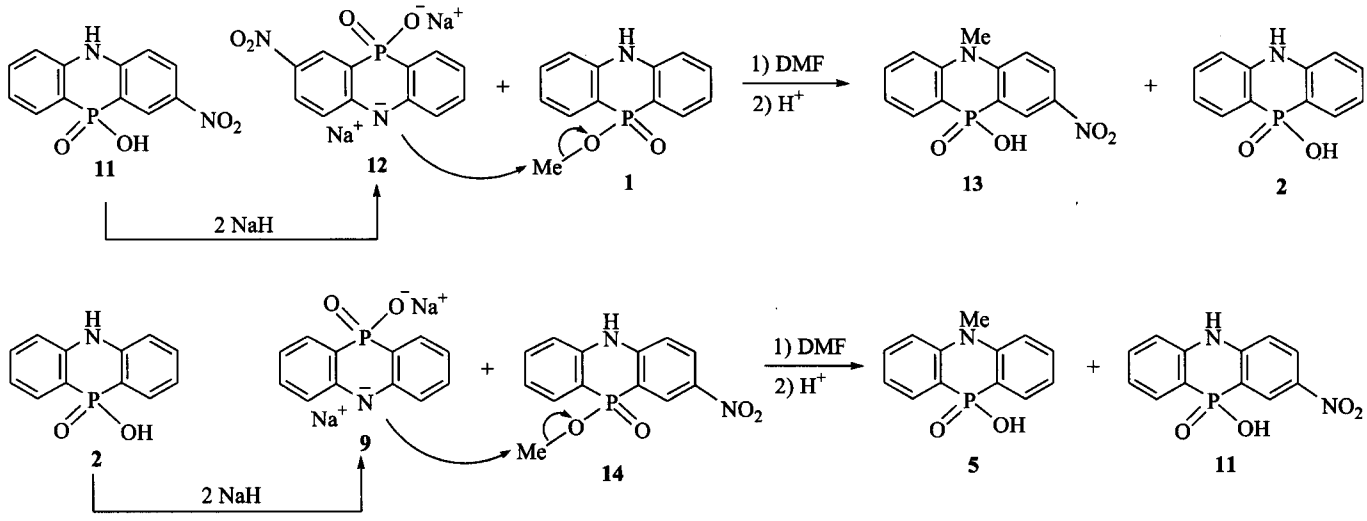
[a] DMF: 40 mL, **1**: 8 mmol, NaH: 8 mmol, reaction time 3.5 h. [b] Analytical conditions were the same as those in Table 1. [c] Reaction time: 2.5 h.

Table 3 Methyl shift results between different compounds

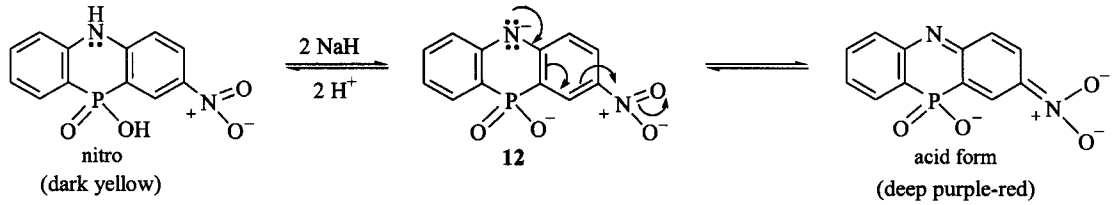
Entry	Reactants (mmol)						Analytical results by HPLC (%)			
	NaH	EtI	**1**	**2**	**11**	**14**	**5**	**8**	**11**	**13**
1[a]	6	3	6	—	—	—	63.63 19.77	32.45 72.21	—	—
2[b]	8	—	4	—	4	—	—	—	40.82	28.23
3[b]	12	—	—	6	—	6	17.15	—	18.23	—

[a] The two products was obtained. Analytical results was obtained from the analysis of HP1100 High Performance Liquid Chromatography/Mass Selective Detector. Analytical conditions: chromatographic column: Hypersil ODS_2 (5 μm, 2.5 mm × 150 mm), mobile phase A: H_2O-HOAc (300 mL/2 mL), mobile phase B: MeOH, flow rate: 0.2 mL/min, using gradient elution analysis, detector wavelength: 254 nm. [b] Analytical conditions were the same as those in Table 1.

Scheme 6 Nucleophilic substitution between different reactants containing 5,10-dihydrophenophosphazine ring system in DMF



Scheme 7 Tautomeric equilibrium between the nitro and its acid form



On the other hand, 10-methoxy-2-nitro-5, 10-dihydrophenophosphazine 10-oxide (**14**) prepared via nitration of **1** in similar way of preparing the nitro compound **11**, reacted with the bis-anion **9** in an equimolar amount, and quite amount of **5** was detected in the crude product (Entry 3 in Table 3). This result further suggested that the mechanism of the methyl migration of **1** was more likely to involve an inter-molecular substitution (Scheme 4) than an intramolecular substitution (Scheme 5).

NMR *of the compounds containing* 5, 10-*dihydrophenophosphazine ring system*

The chemical shifts and multiplicities for ^{1}H and ^{31}P of all compounds containing 5,10-dihydrophenophosphazine ring system involved in the experiment are outlined in Table 4. The compound with NH group afforded one downfield proton signal over δ 10 that should be assigned to NH group because of its disappearance in the corresponding *N*-alkyl compound. Note that *O*-methyl of these compounds exhibited doublet peak due to the coupling between ^{31}P and ^{1}H, and OH group usually appeared in a broad singlet signal at a changeable position or occasionally disappeared. All these characteristics will make it very easy to distinguish *N*-alkyl from *O*-alkyl or NH, OH group, *etc*.

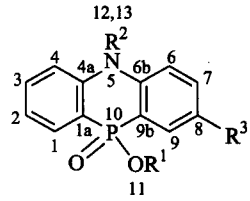
Conclusion

The intermediate **3** obtained from the title compound was treated with NaH at room temperature in anhydrous DMF shifting the methyl group from oxygen to nitrogen atom to form *N*-methyl phosphinic acid as the reaction temperature was increased to 120 ℃. The reaction will be more possibly carried out in a special inter-molecular substitution than intramolecular substitution, *viz.*, the nucleophilic nitrogen anion from one molecule of **1** attacked the carbon atom of the *O*-methyl of another one of **1**.

Experimental

All reagents were commercial products of analytical grade, and the anhydrous DMF was obtained via treatment of commercial DMF following reported method.[9] Melting points were determined with a Mel-Temp capillary melting point apparatus (made in Shanghai, China) and uncorrected, and a Differential Scanning Calorimeter (TA Instruments Ltd. Co., USA). IR spectra were obtained by a FT/IR-430 infrared spectrophotometer (JASCO Ltd. Co., Japan). Analyses of HPLC were performed using an HP1050 Liquid Chromatography (HEWLETT PACKARD Ltd. Co., USA). Mass spectra were taken at CID = 50 ~ 200 V with an HP 1100 System of

Table 4 Chemical shifts (δ)[a] and multiplicities for ^1H and ^{31}P of some compounds containing 5,10-dihydrophenophosphazine ring system



1 R^1 = Me, R^2 = R^3 = H;
2 R^1 = R^2 = R^3 = H;
5 R^1 = R^3 = H, R^2 = Me;
8 R^1 = R^3 = H, R^2 = Et;
11 R^1 = R^2 = H, R^3 = NO_2;
13 R^1 = H, R^2 = Me, R^3 = NO_2;
14 R^1 = Me, R^2 = H, R^3 = NO_2

Compd	1-H/9-H	2-H/8-H	3-H/7-H	4-H/6-H	NH	OH[b]	11-H	12-H	13-H	^{31}P
1	7.73 (q, ^3J = 7.1 Hz)	7.08 (t, ^3J = 7.1 Hz; 6.5 Hz)	7.51 (t, ^3J = 6.5 Hz; 8.1 Hz)	7.23 (t, ^3J = 8.1 Hz)	10.18 (s)	—	3.34 (d, ^3J = 11.9 Hz, 3H)	—	—	19.3
2	7.74 (q, ^3J = 7.2 Hz)	7.04 (t, ^3J = 7.2 Hz; 6.3 Hz)	7.45 (t, ^3J = 6.3 Hz; 8.2 Hz)	7.19 (t, ^3J = 8.2 Hz)	10.09 (s)	~5.9	—	—	—	12.8
5	7.80 (q, ^3J = 7.2 Hz)	7.20 (t, ^3J = 7.2 Hz; 6.5 Hz)	7.58 (t, ^3J = 6.5 Hz; 8.4 Hz)	7.36 (t, ^3J = 8.4 HZ)	—	~4.8	—	3.60 (s, 3H)	—	12.1
8	7.81 (q, ^3J = 7.0 Hz)	7.16 (t, ^3J = 7.0 Hz; 6.4 Hz)	7.58 (t, ^3J = 6.4 Hz; 8.2 Hz)	7.42 (t, ^3J = 8.2 Hz)	—	~5.6	—	4.22 (q, ^3J = 6.8 Hz, 2H)	1.42 (t, ^3J = 6.8 Hz, 3H)	11.9
11	7.78 (q, ^3J = 7.2 Hz)/8.56 (q, ^4J = 2.5 Hz)	7.20 (t, ^3J = 7.2 Hz; 6.7 Hz)	7.55 (q, ^3J = 6.7 Hz; 7.4 Hz)/8.25 (q ^3J = 9.2 Hz; ^4J = 2.5 Hz)	7.27 (t, ^3J = 7.4 Hz)/7.31 (q, ^3J = 9.2 Hz)	10.80 (s)	~4.8	—	—	—	9.2
13	7.80 (q, J = 7.1 Hz)/8.55 (q, ^4J = 2.5 Hz)	7.24 (t, ^3J = 7.1 Hz; 6.7 Hz)	7.61 (t, ^3J = 6.7 Hz; 7.3 Hz)/8.29 (d, ^3J = 8.9 Hz)	7.31—7.35 (m, 2H)	—	~6.8	—	3.89 (s, 3H)	—	9.0
14	7.82 (q, ^3J = 7.1 Hz)/8.58 (q, ^4J = 2.3 Hz)	7.25 (t, ^3J = 7.1 Hz; 6.5 Hz)	7.64 (q, ^3J = 6.5 Hz; 7.3 Hz)/8.32 (q, ^3J = 9.0 Hz; ^4J = 2.3 Hz)	7.34—7.39 (m, 2H)	11.03 (s)	—	3.45 (d, ^3J = 12.0 Hz, 3H)	—	—	16.8

[a] Chemical shifts were expressed in δ value. [b] Broad singlet signal.

HPLC/MS (HEWLETT PACKARD Ltd. Co., USA). ^1H NMR (d^6-DMSO as solvent, TMS as internal standard) and ^{31}P NMR (85% H_3PO_4 as internal standards) spectra were obtained on a Varian INOVA 400 NMR Spectrograph (Varian INOVA Ltd. Co., USA). Elemental analysis was performed by state key laboratory of fine chemicals in Dalian University of Technology on a PE2400 Ⅱ Element Analytical Meter.

Synthesis of 10-*hydroxy*-5,10-*dihydrophenophosphazine* 10-*oxide* (**2**)

The compound **2** was prepared by reported method[6] with yield of 40%, m. p. 271—273 ℃ (lit. 270—272 ℃,[5] 270—274 ℃,[14] and 274—275 ℃[8]); IR (KBr) ν: 3281, 3186, 2270, 1150, 1117, 965 cm^{-1}; MS (CID = 100 V) m/z: 232.1 ($[M + H]^+$), 214.1 ($[M - OH]^+$). Anal. calcd for $C_{12}H_{10}NO_2P$: C 62.34, H 4.36, N 6.06; found C 61.99, H 4.83, N 5.79.

Synthesis of 10-*methoxy*-5,10-*dihydrophenophosphazine* 10-*oxide* (**1**)

A mixture of the phosphinic acid **2** (5 g, *ca*. 0.02 mol) and 25 mL of $SOCl_2$ was stirred at room temperature for 30 min, and then refluxed till the gas of HCl did not give off (approximately 80 min). After cooling the reaction mixture down to room temperature, the yellow-greenish acid chloride was collected by filtration and washed with a little of $SOCl_2$ and then with benzene. The resulting phosphinyl chloride was

added into a three-neck flask and a solution of 2.0 g of NaOMe and 30 mL of MeOH was added. The reaction mixture was refluxed for 2.5 h and cooled down and then poured into 150 mL of ice water, whereupon a cream white precipitate formed. The solid was collected by filtration and washed with ice water to give 3.5 g (*ca.* 71.4%) of **1**, m.p. 220.57 ℃ (It can reach 226.59 ℃ after recrystallization from isopropanol; lit.[8] 224—225 ℃); IR (KBr) ν: 3267, 3221, 2941, 2841, 1165, 951 cm^{-1}; MS (CID = 100 V) *m/z*: 246.1 ($[M+H]^+$), 214.1 ($[M-OMe]^+$).

Syntheses of 10-*hydroxy*-2-*nitro*-5,10-*dihydrophenophosphazine* 10-*oxide* (**11**), 10-*hydroxy*-5-*methyl*-2-*nitro*-5,10-*dihydrophenophosphazine* 10-*oxide* (**13**) *and* 10-*methoxy*-2-*nitro*-5,10-*dihydrophenophosphazine* 10-*oxide* (**14**)

The phosphinic acid **2** (2 g, *ca.* 8.6 mmol) was dissolved into (75 ± 5) mL of HOAc, and then the mixture of 5 mL of conc. HNO_3 and 7 mL of HOAc was added at such a rate that the reaction temperature remained between 9 ℃ and 11 ℃. After being stirred at such temperature for 5 h, the orange-yellow solution was poured into 200 mL of ice water. The yellow precipitate was collected by filtration and washed with distilled water and dried to obtain a dark yellow farinose solid **11** (*ca.* 1.8 g, 74%), m.p. > 300 ℃; IR (KBr) ν: 3261, 3162, 2286, 1529, 1350, 1167, 1130, 959 cm^{-1}; MS (CID = 100 V) *m/z*: 276.2 ($[M]^+$), 229.1 ($[M-HNO_2]^+$).

The nitro compound **13** (a dark yellow farinose solid) and **14** (a brilliant yellow farinose solid) were prepared by substituting **5** and **1** for **2** respectively in above reaction. Melting point of **13** was 286.1—287.8 ℃ (after recrystallization three times from DMF; lit.[15] 288—289 ℃); IR (KBr) ν: 2260, 1531, 1426, 1350, 1181, 947 cm^{-1}; MS (CID = 100 V) *m/z*: 291.1 ($[M+H]^+$), 273.1 ($[M-OH]^+$); 227.1 ($[M-HNO_3]^+$). The compound **14** was melted at 279 ℃ and changed into black; IR (KBr) ν: 3256, 2983, 1528, 1421, 1351, 1180, 950 cm^{-1}; MS (CID = 100 V) *m/z*: 291.1 ($[M+H]^+$), 259.1 ($[M-OMe]^+$), 213.1 ($[M-MeONO_2]^+$).

Methyl migration of **1** *and its experimental verifications*

1 was stirred with anhydrous DMF at room temperature for about 10 min till **1** was completely dissolved. Slightly excessive NaH (60% in mineral oil) was added, which would turn the reaction solution to yellow-green. When hydrogen evolution ceased, the reaction mixture was stirred at proper temperature for 2—4 h. After most of solvent was distilled out under reducing pressure, the reaction mixture was cooled spontaneously, the resultants containing an earth-pale precipitate that was collected by filtration was re-dissolved in 100 mL of water. When a small amount of mineral oil was removed by a separatory funnel, the filtrate was acidified by using dilute HCl to precipitate the milk-white solid, *viz.*, 10-hydroxy-5-methyl-5,10-dihydrophenophosphazine 10-oxide (**5**). This milk-white solid was filtrated and washed with water, and then dried. The melting point of crude product was between 236 ℃ and 245 ℃. But it could reach 250—252 ℃ (lit.[15] 253—254 ℃); IR (KBr) ν: 3245, 2229, 1170, 1133, 965 cm^{-1}; MS (CID = 50 V) *m/z*: 246.1 ($[M+H]^+$), 491.4 ($[M2+H]^+$); MS (CID = 100 V) *m/z*: 246.1 ($[M+H]^+$), 228.1 ($[M-OH]^+$).

To the yellow-green solution of **1** treated with NaH was added half an equimolar amount of EtI and refluxed for 4 h. After removing most of DMF and standing overnight, the white crystal solid was formed at the bottom of the flask. The upper layer of solution was poured into 50 mL of water. Removal of a small amount of mineral oil and then acidification of the filtrate with dilute HCl gave an earth-pale precipitate. The crude earth-pale solid was re-dissolved in water, and carefully acidified to pH = 4—5 to give almost pure compound **8**. M.p. 282.24 ℃ (DSC); IR (KBr) ν: 2985, 2934, 2227, 1169, 1132, 970 cm^{-1}; MS (CID = 50 V) *m/z* (%): 282.0 ($[M+Na]^+$), 260.1 ($[M+H]^+$, 90).

A brown-yellow precipitate was obtained by substituting the compound **11** for **1** and the compound **1** for EtI respectively in above experiment. However, during the reaction, double equimolar amount of NaH (60% in mineral oil) was needed and the compound **1** with the same equimolar amount of **11** was not added to the reaction system in a lump but dropped in a solution of DMF. The resulting crude products with **1**, **2**, **11** and **13** were together analyzed by HPLC. Similarly, when substituting the compound **2** for **11** and the compound **14** for EtI, the new reaction mixture would produce a brown solid. It was analyzed by HPLC together with **2**, **5**, **11** and **13**.

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