Aza-Michael reaction as an efficient method for the synthesis of first representatives of β-azahetaryl-β-diphenylphosphorylalkanones*

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Aza-Michael reaction of (*E*)-4-(diphenylphosphoryl)but-3-en-2-one (**1**) with a number of mono- and bicyclic nitrogen heterocycles proceeds regioselectively in the absence of catalysts with the formation of corresponding β-azahetaryl β-diphenylphosphoryl ketones; in the case of imidazole, the presence of chiral organic catalysts allows one to increase the yields of the adducts and to obtain them in enantiomerically enriched form.

Key words: β-diphenylphosphoryl-α,β-enones, nitrogen heterocycles, aza-Michael reaction, β-azahetaryl-β-diphenylphosphorylalkanones, synthesis, NMR spectra.

Addition process of N-nucleophiles to electron-deficient alkenes by the aza-Michael reaction is not only an efficient method for the formation of carbon—nitrogen bonds in organic compounds, but also meets all the requirements of "green" chemistry.[1] This reaction uses a wide range of Michael acceptors, such as enones, enals, nitro alkenes, *etc.*,[1,2] and catalysts.[3] As to the application of unsaturated organophosphorus compounds as Michael acceptors, the addition of NH-nucleophiles to vinylphosphonates was described for the first time[4] for the reaction of CH_2=CHP(O)$(OEt)_2$ with ammonia, dimethylamine, piperidine, aniline, and diphenylamine. In these examples, in the case of dimethylamine and piperidine no application of any catalysts was required and the reactions proceeded readily at room temperature, leading to the corresponding β-aminoethyl phosphonates $R_2NCH_2CH_2$-P(O)$(OEt)_2$, while in all the other cases the use of a basic catalyst such as sodium methoxide was a necessity. Afterwards, the studies performed by both Russian[5] and foreign scientists[6] resulted in the development of a general approach based on this reaction to the preparation of various representatives of β-aminoethyl phosphonates, phosphinates, and phosphine oxides (additional information can be found in the reviews[1,7]). However, there are no examples of using this methodology for the preparation of nitrogen heterocycles containing ethyl substituents with diarylphosphoryl fragments.

We suggested that the reaction of unsaturated oxoalkyldiphenylphosphine oxides with amino-containing compounds would lead to the synthesis of a new series of corresponding phosphorus- and nitrogen-containing structures, among which it is promising to search for original P,N-ligands and physiologically active compounds. In fact, the nootropic properties of diarylphosphorylacetic acid hydrazides are well known,[8] whereas among nitrogen-containing organophosphorus extractants (carbamoylmethylphosphine oxides[9,10] and N-phosphorylureas[11]) derivatives containing diphenylphosphoryl group possessed the highest efficiency.

As to Michael acceptors, we used recently obtained[12] (*E*)-4-(diphenylphosphoryl)but-3-en-2-one (**1**) and (*E*)-1,5-diphenyl-5-(diphenylphosphoryl)pent-1-en-3-one (**2**). The C=C bond in pentenone **2** is far from the diphenylphosphoryl fragment and is sterically more available for the attack by a nucleophile, than in compound **1**. However, according to the $^{31}P\{^1H\}$ NMR spectral and TLC data, compound **2** does not react with imidazole (**3**), benzimidazole (**4**), 3,5-dimethylpyrazole (**5**), and 1*H*-benzotriazole (**6**), despite a wide variation of the reaction conditions, that indicates a decreased activity of the double bond in this enone. Conversely, in the case of enone **1** the addition reaction of nitrogen heterocycles **3**—**6** proceeds readily enough even in the absence of catalysts, while their presence is usually necessary for the aza-Michael reaction of activated α,β-enones with these substrates to proceed[1] (Scheme 1).

The reaction was carried out under argon upon reflux in anhydrous acetonitrile or toluene (Table 1). As it follows from the analysis of the structure of obtained compounds by ^1H, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ NMR spectroscopy (see Experimental section), the addition proceeds regioselectively at the carbon atom closest to the diphenylphosphoryl group, that is not characteristic of the reac-

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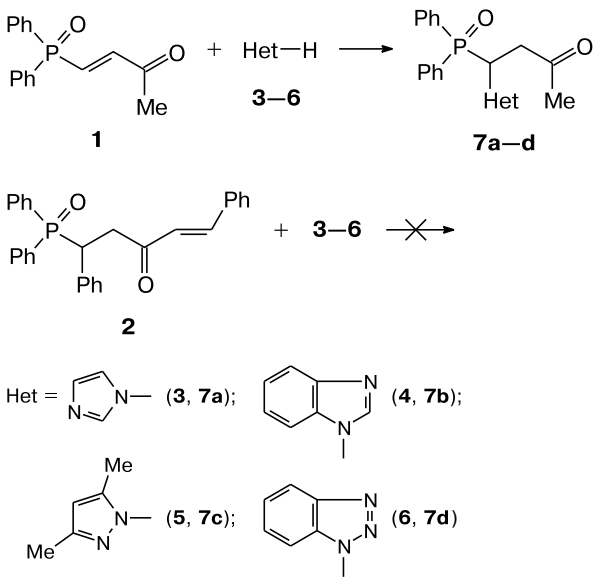
Table 1. Reaction of enone **1** with nitrogen heterocycles **3**—**6**

Hetero-cycle	*T*/°C	τ/h	Solvent	Reaction product	Yield (%)
3	80	15	MeCN	**7a**	78
4	110	16	PhMe	**7b**	37
5	110	65	PhMe	**7c**	80
6	110	48	PhMe	**7d**	41

Note. τ is the reaction time.

Scheme 1



Reagents and conditions: heating, 15—65 h, MeCN ($PhCH_3$).

tion with disubstituted Michael acceptors,[1] and the presence of the second possible regioisomer was not found even in the trace amounts.

These results demonstrate that imidazole **3** turned out to be the most active heterocycle for this process, whereas 3,5-dimethylpyrazole **5** and 1*H*-benzotriazole **6** are the least active in this reaction, that agrees with the data on the basicity (pK_b) of these compounds.

The use of known chiral organocatalysts of Michael reaction such as amino alcohols, diols, and binaphthols[3,13—15] sharply accelerates the reaction of enone **1** and imidazole **3**, as well as increases the yield of the addition product **7**, though, the stereoselectivity of the process is low: the best results (9% *ee*) were obtained with (*S*)-BINOL. The results of the addition of imidazole to enone **1** in the presence of 5 mol.% of chiral catalysts at 110 °C in toluene are given in Table 2. The acceleration of the process by these compounds is probably related to the known possibility of bifunctional catalysis through both the activation of Michael acceptor **1** due to the formation of hydrogen bonds at the carbonyl group and enhancement of nucleophilicity of heterocycle **3** as a result of coordination.[1,3,13—15] The yield was determined based on the results of isolation and analysis of the final Michael product.

The calculations carried out using the PASS program[16] indicate a high (>90%) probability of the presence of nootropic physiological activity for compounds **7a**—**d**.

In summary, the involvement of unsaturated organophosphorus functional compounds in aza-Michael reaction gave earlier unknown representatives of a series of β-hetaryl-β-diphenylphosphorylalkanones, which are of interest as compounds with potential biological activity, phosphorusnitrogen ligands capable of extracting f-elements, and intermediate compounds for the synthesis of various derivatives at the carbonyl group, for example, hydrazones containing pharmacophoric fragments, including alkaloid groups.

Recently,[12,17] we have developed a new approach to the synthesis of phosphorylbutenone **1**, which is based on the reaction of chlorodiphenylphosphine (**8**) with commercially available 4-methoxybut-3-en-2-one (**9**) in the presence of glacial AcOH (the Conant reaction) in anhydrous benzene* at room temperature. This method was considerably more efficient than the known multi-step synthesis of **1**,[19] however, a relatively low rate of Conant reaction under these conditions and environmentally un-

* After publication of the Mikoiajczyk´s work,[18] in which anhydrous benzene was suggested for the first time as a solvent in the Conant reaction, such a version became widely used in the synthesis of diorganylphosphorylalkanones[17] and -alkenones.[12,17]

Table 2. Formation of imidazolyl-substituted ketone **7a** in the presence of chiral catalysts

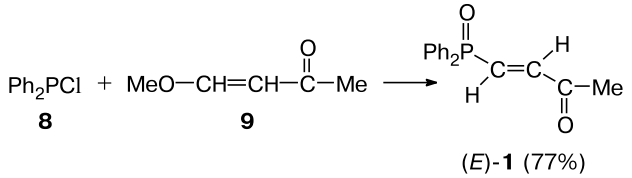
Catalyst	τ/h	Yield **7a** (%)	*ee* **7a** (%)
(4*R*,5*R*)-2,2-Dimethyl-α,α,α´,α´-tetraphenyldioxolane-4,5-dimethanol (TADDOL)	6	53	4
(4*S-trans*)-2,2-Dimethyl-α,α,α´,α´-tetra(1-naphthyl)-1,3-dioxolane-4,5-dimethanol	6	60	4
Cinchonidine	6	68	3
N-Benzyl-(*S*)-proline	6	71	2
(*S*)-(−)-1,1´-Bi(2-naphthol) ((*S*)-BINOL)	21	98	9

Note. τ is the reaction time.

friendly process which uses carcinogenic solvent benzene, stimulated its further improvement.

We found that carrying out the Conant reaction between compound **8** and enone **9** in acetonitrile, rather than benzene, allowed one to simultaneously sharply decrease the reaction time (from 48 h to 1 h) and considerably (by ~20%) increase the yield of phosphorylenone **1** up to 77% (Scheme 2).

Scheme 2



Reagents and conditions: MeCOOH, ~20 °C, 1 h, acetonitrile.

The monitoring of this Conant reaction by $^{31}P\{^1H\}$ NMR spectroscopy showed that a compound with $\delta_P \approx 30$ is initially formed in the course of this process, which is further transformed to phosphorylenone **1**. Since chemical shifts of various 4-diphenylphosphorylated 4-substituted butan-2-ones lie in the range of δ_P 32—34,[17] it can be suggested that the intermediate product of the Conant reaction between compound **8** and enone **9** is a low stable adduct $Ph_2P(O)CH(OMe)CH_2C(O)Me$, which eliminates the methanol molecule to be stereoselectively converted to compound **1**.

In conclusion, based on the Conant reaction we suggested a new considerably more efficient and environmentally friendly approach to the synthesis of *trans*-4-(diphenylphosphoryl)but-3-en-2-one (**1**), which makes this original organophosphorus compound available for wide synthetic practice.

Experimental

^1H, $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AV-400 spectrometer (400,13 MHz (^1H and $^1H\{^{31}P\}$) and 161.98 MHz ($^{31}P\{^1H\}$)) at 30 °C, the solvent was $CDCl_3$. Signals of residual protons of the deuterated solvent were used as an internal reference in the $^1H/^1H\{^{31}P\}$ NMR spectra, 85% aqueous H_3PO_4 was used as an external standard for $^{31}P\{^1H\}$ NMR spectra. IR spectra were recorded on a UR-20 spectrometer in $CHCl_3$. Mass spectra were recorded on a Finnigan SSQ-7000 mass spectrometer. Elemental analysis was performed in the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences. Melting points were measured in a sealed capillary tube using an Electrothermal IA 9000 indicator of melting points. Phosphorylenone **2** was obtained according to the procedure described earlier.[12] The starting azoles **3**—**6**, as well as α,β-enone **9** (Acros) were used without additional purification. Chlorodiphenylphosphine (**8**) (from Acros) was purified by vacuum distillation immediately before use. Glacial acetic acid of reagent grade was distilled before use in reaction. Column chromatography was performed on Al_2O_3 (Brockmann I, 50—200 μm, Acros), silica gel (130—270 mesh, 60 Å, Aldrich), and Florisil® (60—100 mesh) (Acros).

Acetonitrile was dried before use by double distillation over P_2O_5. Other organic solvents used in the work were purified according to the standard procedures.[20]

(*E*)-4-(Diphenylphosphoryl)but-3-en-2-one (1). A solution of glacial AcOH (2.8 g, 46.6 mmol) in anhydrous acetonitrile (5 mL) and a solution of compound **8** (9.1 g, 41.2 mmol) were sequentially added dropwise to a solution of 4-methoxybut-3-en-2-one (**9**) (5.0 g, 49.9 mmol) in anhydrous acetonitrile (15 mL) with stirring on a magnetic stirrer, the stirring was continued for 1 h at room temperature. The solvent and other volatile compounds were removed *in vacuo* (~15 Torr), the residue was allowed to stand *in vacuo* (~1 Torr) for 2.5 h at ~50 °C, a dark red residue was dissolved in CH_2Cl_2 (50 mL) and sequentially filtered through basic Al_2O_3 (9.0 g), silica gel (9.0 g), and Florisil® (9.0 g), every time eluting the support with CH_2Cl_2 (30 mL), the solvent was removed from the filtrate, to the residue was diluted with hexane (35 mL) and refluxed for 2.5 h with stirring on a magnetic stirrer. A precipitate formed was separated, washed with a mixture of hexane—diethyl ether 1 : 1 (3×20 mL), and dried in air until the weight was constant. The yield was 8.816 g (77.4%), m.p. 128—130 °C (*cf.* Ref. 19: m.p. 128—129 °C). Found (%): C, 71.09; H, 5.58; P, 11.35. $C_{16}H_{15}O_2P$. Calculated (%): C, 71.11; H, 5.59; P, 11.46. $^{31}P\{^1H\}$ NMR, δ: 22.87 (s).

4-(Diphenylphosphoryl)-4-(1*H*-imidazol-1-yl)butan-2-one (7a). Imidazole **3** (0.076 g, 1.11 mmol) was added to a solution of (*E*)-4-(diphenylphosphoryl)but-3-en-2-one (**1**) (0.30 g, 1.11 mmol) in acetonitrile (10 mL). The reaction mixture was allowed to stand at 80 °C with continuous stirring on a magnetic stirrer for 15 h. The reaction progress was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Upon completion, the mixture was concentrated to dryness, the product was extracted with diethyl ether. Crystals of the product were formed upon standing of the extract at 0 °C, which were separated and dried at 50 °C in a drying oven until the weight was constant. The yield of **7a** was 0.23 g (53%), m.p. 139—141 °C. An additional amount of the product (0.11 g, 25%) was isolated from the solution. Found (%): C, 67.61; H, 5.74; N, 8.34; P, 9.16. $C_{19}H_{19}N_2O_2P$. Calculated (%): C, 67.45; H, 5.66; N, 8.28; P, 9.15. IR, ν/cm^{-1}: 1203 (P=O), 1719 (C=O). $^{31}P\{^1H\}$ NMR, δ: 30.43 (s). $^1H\{^{31}P\}$ NMR, δ: 2.02 (s, 3 H, Me); 2.93 (dd, 1 H, C$\underline{H}_A$H$_B$, $^3J_{H_A,H}$ = 2.0 Hz, $^2J_{H_A,H_B}$ = 18.4 Hz); 3.34 (dd, 1 H, CH$_A\underline{H}_B$, $^3J_{H_B,H}$ = 10.1 Hz, $^2J_{H_B,H_A}$ = 18.2 Hz); 5.49 (dd, 1 H, PCH, $^3J_{H,H_A}$ = 2.1 Hz, $^3J_{H,H_B}$ = 9.8 Hz); 6.92 (s, 1 H, H_{Het}(4)); 7.15 (s, 1 H, H_{Het}(5)); 7.34 (t, 2 H, *m*-Ph, $^3J_{H,H}$ = 7.6 Hz); 7.45 (t, 1 H, *p*-Ph, $^3J_{H,H}$ = 7.6 Hz); 7.48 (s, 1 H, H_{Het}(2)); 7.48 (d, 2 H, *o*-Ph, $^3J_{H,H}$ = 7.5 Hz); 7.57 (t, 2 H, *m*-Ph, $^3J_{H,H}$ = 7.3 Hz); 7.63 (t, 1 H, *p*-Ph, $^3J_{H,H}$ = 7.3 Hz); 7.88 (d, 2 H, *o*-Ph, $^3J_{H,H}$ = 7.9 Hz).

4-(1*H*-Benzimidazol-1-yl)-4-(diphenylphosphoryl)butan-2-one (7b) was obtained similarly to **7a** from enone **1** (0.10 g, 0.37 mmol) and benzimidazole **4** (0.044 g, 0.37 mmol) in toluene (15 mL) after heating at 110 °C for 16 h. The yield of **7b** was 0.053 g (37 %), m.p. 162—164 °C (Et_2O). Found (%): C, 71.20; H, 5.74; N, 6.51; P, 7.49. $C_{23}H_{21}N_2O_2P$. Calculated (%): C, 71.12; H, 5.45; N, 7.21; P, 7.97. IR, ν/cm^{-1}: 1194 (P=O), 1720 (C=O). $^{31}P\{^1H\}$ NMR, δ: 30.93 (s). ^1H NMR, δ: 1.97 (s, 3 H, Me); 3.16 (ddd, 1 H, C$\underline{H}_A$H$_B$, $^3J_{H_A,H}$ = 3.0 Hz, $^3J_{H_A,P}$ = 8.2 Hz, $^2J_{H_A,H_B}$ = = 18.5 Hz); 3.47 (ddd, 1 H, CH$_A\underline{H}_B$, $^3J_{H_B,H}$ = 9.1 Hz, $^3J_{H_B,P}$ = = 5.0 Hz, $^2J_{H_A,H_B}$ = 18.5 Hz); 5.80—5.86 (m, 1 H, PCH);

7.10—7.30 (m, 5 H, *m*-Ph, *p*-Ph + 2 H_{Het}); 7.44 (dd, 2 H, *o*-Ph, $^3J_{H,H}$ = 7.4 Hz, $^3J_{H,P}$ = 11.4 Hz); 7.55—7.68 (m, 5 H, *m*-, *p*-C_6H_5 + 2 H_{Het}); 7.95 (dd, 2 H, *o*-Ph, $^3J_{H,H}$ = 7.7 Hz, $^3J_{H,P}$ = = 10.2 Hz); 8.20 (br.s, 1 H, $H_{Het}(2)$).

4-(3,5-Dimethylpyrazol-1-yl)-4-(diphenylphosphoryl)butan-2-one (7c). Compound **7c** (0.107 g, 80%) was isolated from the reaction mixture obtained similarly to **7a** from enone **1** (0.10 g, 0.37 mmol) and 3,5-dimethylpyrazole **4c** (0.035 g, 0.37 mmol) in toluene (5 mL) upon heating at 110 °C for 65 h. The product was separated by preparative TLC on silica gel (60 PF_{254} with 30% gypsum) deposited on 180×240-mm glass plate, eluting with a $CHCl_3$: ethyl acetate (1 : 3) solvent mixture, m.p. 170—172 °C. Found (%): C, 68.54; H, 6.04; N, 7.14. $C_{21}H_{23}N_2O_2P$. Calculated (%): C, 68.84; H, 6.33; N, 7.65. IR, ν/cm^{-1}: 1188 (P=O), 1721 (C=O). $^{31}P\{^1H\}$ NMR, δ: 30.82 (s). ^1H NMR, δ: 1.82 (s, 3 H, C(3)$\underline{Me}_{Het}$); 2.05 (s, 3 H, COMe); 2.18 (s, 3 H, C(5)$\underline{Me}_{Het}$); 3.14 (ddd, 1 H, C$\underline{H}_A$H$_B$, $^3J_{H_A,H}$ = 1.8 Hz, $^3J_{H_A,P}$ = 5.8 Hz, $^2J_{H_A,H_B}$ = 18.2 Hz); 3.75 (ddd, 1 H, CH$_A\underline{H}_B$, $^3J_{H_B,H}$ = 10.8 Hz, $^3J_{H_B,P}$ = 4.2 Hz, $^2J_{H_A,H_B}$ = 18.1 Hz); 5.28 (ddd, 1 H, PCH, $^3J_{H,H_A}$ = 1.6 Hz, $^3J_{H,H_B}$ = 10.8 Hz, $^2J_{H,P}$ = 11.1 Hz); 5.56 (s, 1 H, $H(4)_{Het}$); 7.34—7.58 (m, 8 H, *o*-, *m*-Ph, *p*-Ph); 7.99 (dd, 2 H, *o*-Ph, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,P}$ = 11.3 Hz).

4-(1*H*-Benzotriazol-1-yl)-4-(diphenylphosphoryl)butan-2-one (7d) was obtained similarly to **7a** from enone **1** (0.2 g, 0.74 mmol) and 1*H*-benzotriazole **4d** (0.088 g, 0.74 mmol) in toluene (15 mL) after heating at 110 °C for 48 h. The yield of **7d** was 0.12 g (41%), m.p. 148—150 °C. $^{31}P\{^1H\}$ NMR, δ: 30.07 (s). ^1H NMR, δ: 2.07 (s, 3 H, Me); 3.44 (ddd, 1 H, C$\underline{H}_A$H$_B$, $^3J_{H_A,H}$ = = 2.8 Hz, $^3J_{H_A,P}$ = 6.8 Hz, $^2J_{H_A,H_B}$ = 18.4 Hz); 3.90 (ddd, 1 H, CH$_A\underline{H}_B$, $^3J_{H_B,H}$ = 10.1 Hz, $^3J_{H_A,P}$ = 4.8 Hz, $^2J_{H_B,H_A}$ = 18.4 Hz); 6.25—6.32 (m, 1 H, PCH); 7.25—7.29 (m, 1 H, $H(5)_{Het}$); 7.32—7.55 (m, 7 H, *m*-Ph, *p*-Ph + $H_{Het}(6)$); 7.61 (d, 1 H, $H_{Het}(7)$, $^3J_{H,H}$ = = 8.4 Hz); 7.70—7.83 (m, 4 H, *o*-Ph); 7.92 (d, 1 H, $H_{Het}(4)$, $^3J_{H,H}$ = 8.3 Hz). MS [CH_3CN]: 390.1363 $[M + H]^+$; 412.1188 $[M + Na]^+$. Calculated for $C_{22}H_{21}N_3O_2P$ 390.137140; calculated for $C_{22}H_{20}N_3NaO_2P$ 412.119085.

The aza-Michael reaction of imidazole **3** with (*E*)-4-(diphenylphosphoryl)but-3-en-2-one (**1**) was carried out in the presence of 5 mol.% of the chiral catalysts. The mixture was concentrated and the product was analyzed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and by HPLC on a chiral column (HPLC analysis (Aligent) Daicel Chiracel OD-H column; eluent: hexane—isopropyl alcohol (95 : 15) + 0.2% Et_2NH; 0.75 mL min^{-1}, UV-detector 225 nm).

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