SYNTHESIS OF DIETHYL 1,2,3-TRIAZOLEALKYL-PHOSPHONATES THROUGH 1,3-DIPOLAR CYCLOADDITION OF AZIDES WITH ACETYLENES

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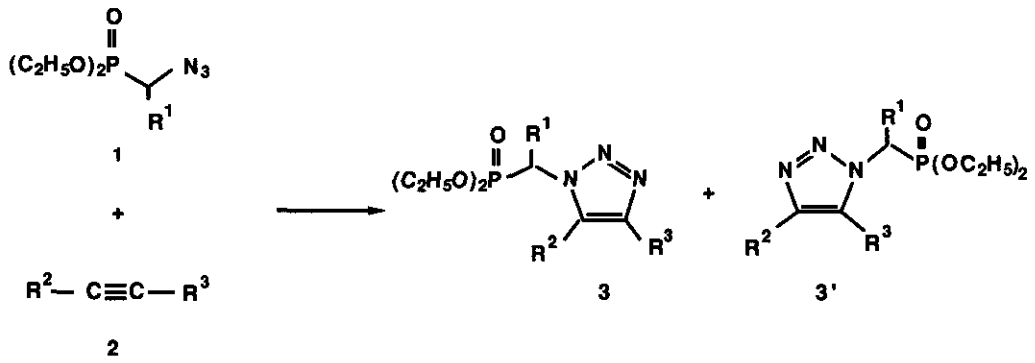
Abstract - 4,5-Disubstituted 1-(diethoxyphosphorylmethyl)-1,2,3-triazoles were prepared through thermal 1,3-dipolar cycloaddition of diethyl azidoalkylphosphonates with alkynes.

1,2,3-Triazoles have received much attention because of their range of applications, not only for their theoretical interest and synthetic value[1] but also for their utility in agriculture[2] as fungicides,[3,4] herbicides,[4] and industry as light stabilizers,[5] fluorescent whiteners,[6] optical brightening agents and corrosion retardants.[7-9] Moreover, 1,2,3-triazole derivatives show significant antimicrobial,[10] cytostatic,[11-14] virostatic,[15] and antiinflamatory[16] activity.

In addition, the biological activity[17,18] of α-aminophosphonic acid analogues of the naturally occurring amino acids and their derivatives has resulted in a considerable research effort directed towards developing suitable synthetic methodologies for their preparation. In recent years, we have been involved in the chemistry of phosphazenes [19] obtained from azides and phosphines as well as their utility in the preparation of acyclic[20] and heterocyclic[21] compounds. Therefore, it was considered worth exploring the synthesis of functionalized 1,2,3-triazoles derived from α-aminophosphonates.

1,3-Dipolar cycloadditions are an excellent tool in the construction of five membered heterocycles,[22,23] and one of the most versatile synthetic routes to triazoles involves the ring formation through thermal 1,3-dipolar cycloaddition of azides and alkynes.[23] However, it was felt that certain variations in the azides might permit easier refunctionalization of the resultant cycloadducts. In this context, it is worth noting that very few reports have been published of the cycloaddition reactions of phosphorus functionalized 1,3-dipoles as well as some synthetic applications of their cycloadducts.[24] Therefore, we report here what is, an example of an intermolecular cycloaddition reaction of phosphorus functionalized azides and alkynes leading to substituted triazoles derived from phosphonates.



When diethyl azidomethylphosphonate[25] (**1**) was allowed to react with an equimolecular amount of dimethyl acetylenedicarboxylate (**2**, $R^2 = R^3 = CO_2CH_3$) and dibenzoylacetylene (**2**, $R^2 = R^3 = COC_6H_5$) in refluxing toluene, 1-phosphonomethyl-1,2,3-triazoles (**3a**) and (**3b**) were respectively obtained in good yields. Similarly, other azidomethylphosphonates (**1**) reacted with electron-withdrawing substituted alkynes, such as carboxylic acid esters (methyl propiolate, methyl butynoate, ethyl phenylpropiolate) and phosphorus containing acetylenes (phosphine oxide and phosphonates) in toluene at reflux to give 1-(diethoxyphosphorylalkyl)-1,2,3-triazole (**3c-o**) and (**3'c-o**). Regioisomeric cycloadducts (**3**) and (**3'**) were isolated by means of short flash column chromatography with *n*-hexane/ether as eluent. Yields and regioisomers ratio are given in Table **1.**

The structure of compounds (**3**) and (**3'**) is supported by the spectroscopic data. Thus, the ^{31}P-nmr spectrum of the crude reaction mixture (**3**), (**3'g**) showed absorptions in an approximate regioisomer ratio of 50 : 50 as indicated by the relative peak areas for each compound. Further examination of the ^{1}H and ^{13}C-nmr spectra was consistent with the structure of both isomers. Then, in the ^{1}H-nmr spectrum of compound (**3g**) methylene protons resonate at δ_H 5.00 as well-resolved doublets with coupling constants of ($^{2}J_{PH}$ = 13.6 Hz) and the methyl group gives a singlet at δ_H 2.26, while the ^{13} C-nmr spectrum shows an absorption at δ_C 45.42 ($^{1}J_{PC}$ = 153 Hz) assignable to the carbon bound to phosphorus. In addition, selective irradiation at the frequency of the methyl signal resulted in an NOE. enhancement of the doublet at δ_H 5.00. This result supports the proposed structure for regioisomer (**3g**). Conversely, compound (**3'g**) showed clearly different absorption, namely a doublet at δ_H 4.68 ($^{2}J_{PH}$ = 12.7 Hz) for the methylene protons as well as a high-field signal for the methyl group at δ_H 2.59, while in the ^{13}C-nmr spectrum the absorption of the methylene carbon was shifted to higher field δ_C 44.10, with a higher value of the phosphorus-carbon coupling constant ($^{1}J_{PC}$ = 155 Hz) relative to the other regioisomer, which supports the proposed structure of triazole (**3'g**).

Table 1: 1,2,3-Triazole derivatives obtained.

Compound	R^1	R^2	R^3	Yield (%)	Ratio (**3** : **3'**)[a]
3a	H	CO_2CH_3	CO_2CH_3	92	
3b	H	COC_6H_5	COC_6H_5	85	
3/3'c	H	H	CO_2CH_3	86	25 : 75
3/3'd	H	CH_3	CO_2CH_3	85	44 : 56
3/3'e	H	C_6H_5	$CO_2C_2H_5$	83	50 : 50
3/3'f	H	CH_3	$PO(C_6H_5)_2$	80	40 : 60
3/3'g	H	CH_3	$PO(OC_2H_5)_2$	82	50 : 50
3/3'h	CH_3	H	CO_2CH_3	90	20 : 80
3/3'i	CH_3	CH_3	CO_2CH_3	89	50 : 50
3/3'j	CH_3	C_6H_5	$CO_2C_2H_5$	86	35 : 65
3/3'k	CH_3	CH_3	$PO(OC_2H_5)_2$	85	49 : 51
3/3'l	C_6H_5	H	CO_2CH_3	95	18 : 82
3/3'm	C_6H_5	CH_3	CO_2CH_3	83	45 : 55
3/3'n	C_6H_5	C_6H_5	$CO_2C_2H_5$	85	46 : 54
3/3'o	C_6H_5	CH_3	$PO(OC_2H_5)_2$	90	52 : 48

[a] Determined by ^{31}P-nmr from crude reaction mixtures.

In conclusion, an example of intermolecular [3+2] cycloaddition reaction of azidoalkylphosphonates is reported. This reaction leads to a convenient method for the synthesis of polysubstituted 1,2,3-triazoles derived from phosphonates (**3**).

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EXPERIMENTAL

Column chromatography was carried out on silica gel (Merck, 70-230 mesh) with a mixture of hexane-ether as eluent. Melting points were determined with a Buchi SMP-20 apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR 42-40 spectrophotometer, and band frecuencies are reported in cm^{-1}. ^1H and ^{13}C-nmr and N O E. experiment were recorded on a Bruker 250 MHz spectrometer in $CDCl_3$ as solvent. Chemical shifts were reported downfield from TMS as an internal reference for ^1H-nmr spectra and $CDCl_3$ for ^{13}C-nmr spectra (abbreviations used: s singlet; d doublet; t triplet; q quartet; qu quintet; m multiplet; dd doublet of doublets). ^{31}P-nmr spectra were obtained on a Varian VXR 300 MHz spectrometer using phosphoric acid 85 % as an internal reference. Mass spectra were obtained on a Hewlett Packard 5890 espectrometer. Microanalyses were performed in a Perkin Elmer model 240 instrument.

Preparation of 1,2,3-Triazoles (3a) and (3b).

To a solution of dimethyl acetylenedicarboxylate or dibenzoylacetylene (**2**) (3 mmol) in toluene (10 ml) was added dropwise with stirring a solution of diethyl 1-azidoalkylphosphonate[25] (**1**) (3 mmol) in toluene (20 ml), the reaction mixture was heated at reflux for 30-40 h, cooled and evaporated. Crude residue was purified by flash column cromatography with *n*-hexane/ether (1:1) as eluent to give product (**3**).

1-(Diethoxyphosphorylmethyl)-4,5-bis(methoxycarbonyl)-1,2,3-triazole *(**3a**): Obtained as white solid.* Recrystallized from a mixture of CH_2Cl_2/hexane; mp 83-84 °C; ^1H-nmr, δ_H: 1.20 (t, $^3J_{HH}$ = 7.1 Hz, 6H), 3.88 (s, 3H), 3.92 (s, 3H), 4.03 (m, 4H), 5.04 (d, $^2J_{PH}$ = 13.2 Hz, 2H) ppm; ^{13}C-nmr, δ_H: 15.9, 45.3 (d, $^1J_{PC}$ = 153.2 Hz), 52.4, 53.2, 63.3, 130.4, 139.6, 158.5, 159.9 ppm; ^{31}P-nmr, δ_P: 15.56 ppm; ms, *m/z*: 307 (M^+ - N_2, 36%); ir, υ: 1737, 1731, 1460, 1247, 1053 cm^{-1}; Anal. Calcd for $C_{11}H_{18}N_3O_7P$: C, 39.39; H, 5.41; N, 12.54. Found: C, 39.42; H, 5.49; N, 12.60.

4,5-Dibenzoyl(diethoxyphosphorylmethyl)-1,2,3-triazole (3b): Obtained as syrup; R_f (ethyl acetate): 0.58; ^1H-nmr, δ_H: 1.11 (t, $^3J_{HH}$ = 7.1 Hz, 6H), 3.99 (m, 4H), 5.05 (d, $^2J_{PH}$ = 12.9 Hz, 2H), 7.25-8.15 (m, 10H) ppm; ^{13}C-nmr, δ_C: 15.9, 44.4 (d, $^1J_{PC}$ = 151.7 Hz), 63.2, 128.3-136.1, 137.1, 147.1, 184.9, 185.8 ppm; ^{31}P-nmr, δ_P: 15.86 ppm; ms, *m/z*: 427 (M^+, 5%); ir, υ: 1664, 1500, 1250, 1240, 1060, 1020 cm^{-1}; Anal. Calcd for $C_{21}H_{22}N_3O_5P$: C, 58.99; H, 5.19; N, 9.83. Found: C, 59.22; H, 5.29; N, 9.90.

Preparation of Substituted 1,2,3-Triazoles (3/3' c-o).

To a solution of alkyne (**2**) (3 mmol) in toluene (10 ml) was added dropwise with stirring a solution of diethyl 1-azidoalkylphosphonate[25] (**1**) (3 mmol) in toluene (20 ml), the reaction mixture was heated at reflux for 30-40 h. Concentration in vacuum gave the mixture of the two regioisomeric cycloadducts (**3**) and (**3'**) isolated by flash column chromatography (silica gel; eluent: *n*-hexane-ether).

1-(Diethoxyphosphorylmethyl)-4-methoxycarbonyl-1,2,3-triazole (3c): Obtained as syrup; R_f (ethyl acetate): 0.35; ^1H-nmr, δ_H: 1.29 (t, $^3J_{HH}$ = 7.1 Hz, 6H), 3.93 (s, 3H), 4.13 (m, 4H), 5.24 (d, $^2J_{PH}$ = 13.5 Hz, 2H), 8.11 (s, 1H) ppm; ^{13}C-nmr, δ_C: 16.2, 45.4 (d, $^1J_{PC}$ = 153.4 Hz), 52.6, 63.2, 128.3, 137.5, 158.8 ppm; ^{31}P-nmr, δ_P: 16.15 ppm; ms, *m/z*: 278 (M^++ 1, 12%); Anal. Calcd for $C_9H_{16}N_3O_5P$: C, 38.97; H, 5.82; N, 15.16. Found: C, 39.17; H, 5.69; N, 15.08.

1-(Diethoxyphosphorylmethyl)-5-methoxycarbonyl-1,2,3-triazole (3'c): Obtained as white solid. Recrystallized from a mixture of CH_2Cl_2/hexane; mp 85-86°C; R_f (ethyl acetate): 0.27; ^{1}H-nmr, δ_H : 1.26 (t, $^3J_{HH}$ = 7.0 Hz, 6H), 3.90 (s, 3H), 4.10 (m, 4H), 4.79 (d, $^2J_{PH}$ = 13.2 Hz, 2H), 8.28 (s, 1H) ppm; ^{13}C-nmr, δ_C : 16.1, 45.9 (d, $^1J_{PC}$ = 155.1 Hz), 52.1, 63.6, 128.5, 140.1, 160.7 ppm; ^{31}P-nmr, δ_P : 15.79 ppm; ms, *m/z*: 249 (M^+ - N_2, 17%); ir, υ: 1731, 1460, 1255, 1210, 1040, 1015 cm^{-1}, Anal. Calcd for $C_9H_{16}N_3O_5P$: C, 38.97; H, 5.82; N, 15.16. Found: C, 39.14; H, 5.73; N, 15.07.

1-(Diethoxyphosphorylmethyl)-5-methyl-4-methoxycarbonyl-1,2,3-triazole (3d): Obtained as syrup; R_f (ethyl acetate): 0.36; ^{1}H-nmr, δ_H : 1.26 (t, $^3J_{HH}$ = 7.0 Hz, 6H), 2.51 (s, 3H), 4.02 (s, 3H), 4.10 (m, 4H), 5.18 (d, $^2J_{PH}$ = 13.4 Hz, 2H) ppm; ^{13}C-nmr, δ_C : 11.3, 16.3, 45.7 (d, $^1J_{PC}$ = 153.4 Hz), 52.4, 63.2, 130.4, 137.5, 162.9 ppm; ^{31}P-nmr, δ_P : 16.82 ppm; ms, *m/z*: 291 (M^+, 5%); Anal. Calcd for $C_{10}H_{18}N_3O_5P$: C, 41.22; H, 6.23; N, 14.43. Found: C, 41.35; H, 6.35; N, 14.55. **1-(Diethoxyphosphorylmethyl)-4-methyl-5-methoxycarbonyl-1,2,3-triazole (3'd)**: Obtained as syrup; R_f (ethyl acetate): 0.27; ^{1}H-nmr, δ_H : 1.28 (t, $^3J_{HH}$ = 7.0 Hz, 6H), 2.63 (s, 3H), 3.92 (s, 3H), 4.10 (m, 4H), 4.68 (d, $^2J_{PH}$ = 12.6 Hz, 2H) ppm; ^{13}C-nmr, δ_C : 9.1, 16.2, 44.0 (d, $^1J_{PC}$ = 156.6 Hz), 51.9, 63.6, 131.7, 139.8, 159.5 ppm; ^{31}P-nmr, δ_P : 16.50 ppm; ms, *m/z*: 291 (M^+, 62%); ir, υ: 1723, 1450, 1243, 1016 cm^{-1}; Anal. Calcd for $C_{10}H_{18}N_3O_5P$: C, 41.22; H, 6.23; N, 14.43. Found: C, 41.35; H, 6.35; N, 14.55.

1-(Diethoxyphosphorylmethyl)-4-ethoxycarbonyl-5-phenyl-1,2,3-triazole (3e): Obtained as syrup; R_f (ethyl acetate): 0.37; ^{1}H-nmr, δ_H : 1.24 (m, 9H), 4.10 (m, 4H), 4.31 (m, 2H), 5.21 (d, $^2J_{PH}$ = 13.2 Hz, 2H), 7.35 (m, 5H) ppm; ^{13}C-nmr, δ_C : 13.7, 16.1, 45.9 (d, $^1J_{PC}$ = 153.4 Hz, 2H), 62.1, 63.4, 127.9-129.3, 125.0, 149.8, 159.1 ppm; ^{31}P-nmr, δ_P : 16.88 ppm; ms, *m/z*: 367 (M^+, 7%); Anal. Calcd for $C_{16}H_{22}N_3O_5P$: C, 52.29; H, 6.04; N, 11.44. Found: C, 52.17; H, 6.01; N, 11.37. **1-(Diethoxyphosphorylmethyl)-5-ethoxycarbonyl-4-phenyl-1,2,3-triazole (3'e)**: Obtained as syrup; R_f (ethyl acetate): 0.30; ^{1}H-nmr, δ_H : 1.11 (m, 9H), 3.94 (m, 4H), 4.15 (m, 2H), 4.50 (d, $^2J_{PH}$ = 13.2 Hz, 2H), 7.36 (m, 5H) ppm; ^{13}C-nmr, δ_C : 13.9, 16.1, 43.7 (d, $^1J_{PC}$ = 155.1 Hz, 2H), 60.8, 63.3, 125.3, 141.8, 160.5 ppm; ^{31}P-nmr, δ_P : 16.33 ppm; ms, *m/z*: 367 (M^+, 7%); ir, υ: 1721, 1480, 1250, 1210, 1020 cm^{-1}; Anal. Calcd for $C_{16}H_{22}N_3O_5P$: C, 52.29; H, 6.04; N, 11.44. Found: C, 52.33; H, 6.11; N, 11.47.

1-(Diethoxyphosphorylmethyl)-4-diphenylphosphoryl-5-methyl-1,2,3-triazole (3f): Obtained as syrup; R_f (ethyl acetate): 0.13; ^{1}H-nmr, δ_H : 1.20 (m, 6H), 1.77 (s, 3H), 4.06 (m, 4H), 5.40 (d, $^2J_{PH}$ = 13.6 Hz, 2H), 7.48-7.66 (m, 10H); ^{13}C-nmr, δ_C 12.2, 16.2, 45.6 (d, $^1J_{PC}$ = 152.3 Hz), 63.1, 124.5 (d, $^1J_{PC}$ = 113.7 Hz), 128.8-133.2, 130.7, 148.6 (d, $^2J_{PC}$ = 15.7 Hz); ^{31}P-nmr, δ_P : 20.81, 17.57 ppm; ms, *m/z*: 404 (M^+ - N_2, 6%); Anal. Calcd for $C_{20}H_{25}N_3O_4P_2$: C, 55.41; H, 5.82; N, 9.70. Found: C, 55.52; H, 5.87; N, 9.62. **1-(Diethoxyphosphorylmethyl)-5-diphenylphosphoryl-4-methyl-1,2,3-triazole (3'f)**: Obtained as syrup; R_f (ethyl acetate): 0.10; ^{1}H-nmr, δ_H : 1.05 (m, 6H), 2.40 (s, 3H), 3.87 (m, 4H), 4.52 (d, $^2J_{PH}$ = 12.7 Hz, 2H), 7.18-7.65 (m, 10H); ^{13}C-nmr, δ_C: 8.6, 16.2, 43.5 (d, $^1J_{PC}$ = 155.5 Hz), 63.2, 128.2-131.9, 133.6 (d, $^1J_{PC}$ = 268 Hz), 142.2 (d, $^2J_{PC}$ = 25.1 Hz); ^{31}P-nmr, δ_P: 20.77, 17.60 ppm; ms, *m/z*: 404 (M^+, 2%); ir, υ: 1440, 1250, 1190, 1020 cm^{-1}; Anal. Calcd for $C_{20}H_{25}N_3O_4P_2$: C, 55.41; H, 5.82; N, 9.70. Found: C, 55.49; H, 5.89; N, 9.75.

4-Diethoxyphosphoryl-1-(1-diethoxyphosphoryl-1-methylmethyl)-5-methyl-1,2,3-triazole (3g): Obtained as syrup; R_f (ethyl acetate): 0.20; ^{1}H-nmr, δ_H : 1.15 (m, 12H), 2.26 (s, 3H), 4.00 (m, 8H), 5.00 (d, $^2J_{PH}$ = 13.6 Hz, 2H); ^{13}C-nmr, δ_C . 11.4, 16.2, 45.4 (d, $^1J_{PC}$ = 154.0), 63.2, 122.5 (d, $^1J_{PC}$ = 219.6 Hz), 150.0 (d, $^2J_{PC}$ = 20.6 Hz); ^{31}P-nmr, δ_P: 17.35, 5.12 ppm; ms, *m/z*: 369 (M^+, 10%); Anal. Calcd for $C_{12}H_{25}N_3O_4P_2$: C, 39.01; H, 6.83; N, 11.38. Found: C, 39.11; H, 6.86; N,

11.29. ***5-Diethoxyphosphoryl-1-(diethoxyphosphoryl-1-methylmethyl)-4-methyl-1,2,3-triazole*** **(3'g)**: Obtained as syrup; R_f (ethyl acetate): 0.12; ^{1}H-nmr, δ_H : 1.32 (m, 12H), 2.59 (s, 3H), 4.17 (m, 8H), 4.68 (d, $^2J_{PH}$ = 12.7 Hz, 2H); ^{13}C-nmr, δ_C: 8.7, 16.1, 44.1 (d, $^1J_{PC}$ = 155.5 Hz), 63.3, 132.1 (d, $^1J_{PC}$ = 238 Hz), 142.0 (d, $^2J_{PC}$ = 26 Hz); ^{31}P-nmr, δ_P : 16.12, 7.93 ppm; ms, *m/z*: 369 (M^+, 9%); ir, υ: 1440, 1245, 1015 cm^{-1}; Anal. Calcd for $C_{12}H_{25}N_3O_4P_2$: C, 39.01; H, 6.83; N, 11.38. Found: C, 39.09; H, 6.89; N, 11.42.

1-(1-Diethoxyphosphoryl-1-methylmethyl)-4-methoxycarbonyl-1,2,3-triazole (3h): Obtained as syrup; R_f (ethyl acetate): 0.27; ^{1}H-nmr, δ_H: 1.25 (m, 6 H), 1.91 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 16.0 Hz, 3H), 3.91 (s, 3H), 4.11 (m, 4H), 5.90 (m, 1H), 8.11 (s, 1H); ^{13}C-nmr, δ_C: 15.5, 16.3, 52.2 (d, $^1J_{PC}$ = 155.2, Hz), 52.5, 63.5, 129.9, 137.6, 159.8; ^{31}P-nmr, δ_P: 19.41 ppm; ms, *m/z*: 263 (M^+- N_2, 13%); Anal. Calcd for $C_{10}H_{18}N_3O_5P$: C, 41.22; H, 6.23; N, 14.43. Found: C, 41.20; H, 6.12; N, 14.45. **1-(1-Diethoxyphosphoryl-1-methylmethyl)-5-methoxycarbonyl-1,2,3-triazole (3'h)**: Obtained as syrup; R_f (ethyl acetate): 0.20; ^{1}H-nmr, δ_H: 1.19 (m, 6H), 1.74 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 16.0 Hz, 3H), 3.81 (s, 3H), 4.04 (m, 4H), 5.05 (m, 1H), 8.23 (s, 1H); ^{13}C-nmr, δ_C: 15.8, 16.1, 52.1, 53.3 (d, $^1J_{PC}$ = 155.8 Hz), 63.5, 127.0, 140.0, 160.8; ^{31}P-nmr, δ_P : 19.55 ppm; ms, *m/z*: 291 (M^+, 11%); ir, υ: 1733, 1440, 1258, 1202, 1110, 1020 cm^{-1}; Anal. Calcd for $C_{10}H_{18}N_3O_5P$: C, 41.22; H, 6.23; N, 14.43. Found: C, 41.27; H, 6.30; N, 14.49.

1-(1-Diethoxyphosphoryl-1-methylmethyl)-5-methyl-4-methoxycarbonyl-1,2,3-triazole (3i): Obtained as syrup; R_f (ethyl acetate): 0.29; ^{1}H-nmr, δ_H : 1.05 (t, $^3J_{HH}$ = 7.3 Hz, 6H), 1.68 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 15.9 Hz, 3H), 2.29 (s, 3H), 3.72 (s, 3H), 3.87 (m, 4H), 5.66 (m, 1H); ^{13}C-nmr, δ_C : 8.9, 15.3, 6.1, 52.2, 53.4 (d, $^1J_{PC}$ = 155.2 Hz), 63.2, 125.8, 147.6, 159.7; ^{31}P-nmr, δ_P: 19.99 ppm; ms, *m/z*: 305 (M^+, 2%); Anal. Calcd for $C_{11}H_{20}N_3O_5P$: C, 43.26; H, 6.61; N, 13.77. Found: C, 43.31; H, 6.59; N, 13.80. ***1-(1-Dimetoxyphosphoryl-1-methylmethyl)-4-methyl-5-methoxycarbonyl-1,2,3-triazole*** **(3'i)**: Obtained as syrup; R_f (ethyl acetate): 0.22; ^{1}H-nmr, δ_H : 12.07 (t, $^3J_{HH}$ =7.4 Hz, 6H), 1.70 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 16.1 Hz, 3H), 2.43 (s, 3H), 3.70 (s, 3H), 3.90 (m, 4H), 4.57 (m, 1H); ^{13}C-nmr, δ_C : 12.3, 14.9, 16.1, 51.6, 52.6 (d, $^1J_{PC}$ = 157.4 Hz), 63.6, 135.9 , 139.2, 161.8; ^{31}P-nmr, δ_P: 19.33 ppm; ms, *m/z*: 305 (M^+, 21%); ir, υ: 1725, 1460, 1230, 1020 cm^{-1}; Anal. Calcd for $C_{11}H_{20}N_3O_5P$: C, 43.26; H, 6.61; N, 13.77. Found: C, 43.35; H, 6.68; N, 13.83.

1-(1-Diethoxyphosphoryl-1-methylmethyl)-4-ethoxycarbonyl-5-fenyl-1,2,3-triazole (3j): Obtained as syrup; R_f (ethyl acetate): 0.60; ^{1}H-nmr, δ_H : 1.25 (m, 9H), 1.92 (dd, $^3J_{HH}$= 7.5 Hz, $^3J_{PH}$ = 16.1 Hz, 3H), 4.14 (m, 4H), 4.27 (m, 2H), 5.84 (m, 1H), 7.34-7.68 (m, 5H); ^{13}C-nmr, δ_C : 13.5, 15.3, 16.2, 53.0 (d, $^1J_{PC}$ = 155.3 Hz), 61.8, 63.3, 124.8, 129.3-130.1, 149.5, 159.3; ^{31}P-nmr, δ_P : 19.96 ppm; ms, *m/z*: 381 (M^+, 14%); Anal. Calcd for $C_{17}H_{24}N_3O_5P$: C, 53.52; H, 6.35; N, 11.02. Found: C, 53.47; H, 6.39; N, 11.09. **1-(1-Diethoxyphosphoryl-1-methylmethyl)-5-ethoxycarbonyl-4-fenyl-1,2,3-triazole (3'j)**: Obtained as syrup; R_f (ethyl acetate): 0.40; ^{1}H-nmr, δ_H: 1.29 (m, 9H), 1.80 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 15.8 Hz, 3H), 4.12 (m, 4H), 4.30 (m, 2H), 4.57 (m, 1H), 7.48 (m, 5H); ^{13}C-nmr, δ_C : 14.1, 16.4, 16.6, 51.8 (d, $^1J_{PC}$ = 157.0 Hz), 61.0, 64.0, 128.7, 130.1-133.3, 139.5, 162.5; ^{31}P-nmr, δ_P : 19.37 ppm; ms, *m/z*: 381 (M^+, 3%); ir, υ: 1723, 1450, 1240, 1212, 1016 cm^{-1}; Anal. Calcd for $C_{17}H_{24}N_3O_5P$: C, 53.52; H, 6.35; N, 11.02. Found: C, 53.58; H, 6.40; N, 11.07.

4-Diethoxyphosphoryl-1-(1-diethoxyphosphoryl-1-methylmethyl)-5-methyl-1,2,3-triazole (3k): Obtained as syrup; R_f (ethyl acetate): 0.23; ^{1}H-nmr, δ_H : 1.29 (m, 12H), 1.79 (dd, $^3J_{HH}$ = 7.2.Hz, $^3J_{PH}$ = 15.9 Hz, 3H), 2.42 (s, 3H), 4.12 (m, 8H), 5.69 (m, 1H); ^{13}C-nmr, δ_C: 1.2, 16.1, 16.3, 52.3 (d, $^1J_{PC}$ = 155.7 Hz), 62.9, 122.6 (d, $^1J_{PC}$ = 217.6 Hz), 149.6 (d, $^2J_{PC}$ = 20.3 Hz); ^{31}P-nmr, δ_P : 20.26, 5.43 ppm; ms, *m/z*: 383 (M^+, 7%); Anal. Calcd for $C_{13}H_{27}N_3O_6P_2$: C, 40.72; H, 7.10; N, 10.96.

Found: C, 40.80; H, 7.20; N, 11.03. **5-Diethoxyphosphoryl-1-(diethoxyphosphoryl-1-methylmethyl)-4-methyl-1,2,3-triazole (3'k)**: Obtained as syrup; R_f (ethyl acetate): 0.17; ^{1}H-nmr, δ_H : 1.22 (m, 12H), 1.86 (dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{PH}$ = 16.1 Hz), 2.52 (s, 3H), 4.10 (m, 8H), 4.66 (m, 1H); ^{13}C- nmr, δ_C: 8.5, 15.1, 16.0, 51.2 (d, $^1J_{PC}$ = 157.5 Hz), 62.6, 63.4, 131.9 (d, $^1J_{PC}$ = 238.7 Hz), 141.2 (d, $^2J_{PC}$ = 34,8 Hz); ^{31}P-nmr, δ_P : 19.48, 8.26 ppm; ms, *m/z*: 383 (M^+, 11%); ir, υ: 1450, 1258, 1020 cm^{-1}; Anal. Calcd for $C_{13}H_{27}N_3O_6P_2$: C, 40.72; H, 7.10; N, 10.96. Found: C, 40.68; H, 7.22; N, 11.01.

1-(1-Diethoxyphosphoryl-1-phenylmethyl)-4-methoxycarbonyl-1,2,3-triazole (3l): Obtained as syrup; R_f (ethyl acetate): 0.38; ^{1}H-nmr, δ_H : 1.18 (m, 6H), 3.80 (s, 3H), 4.08 (m, 4H), 6.96 (d, $^2J_{PH}$ = 22.0 Hz, 1H), 7.50 (m, 5H), 8.12 (s, 1H); ^{13}C-nmr, δ_C : 15.9, 52.3, 61.4 (d, $^1J_{PC}$ = 153.3 Hz), 63.6, 128.4-130.0, 132.0, 137.3, 158.5; ^{13}P-nmr, δ_P : 15.68 ppm; ms, *m/z*: 325 (M^+ -N_2, 15%); Anal. Calcd for $C_{15}H_{20}N_3O_5P$: C, 50.97; H, 5.71; N, 11.90. Found: C, 50.89; H, 5.78; N, 11.86. **1-(1-Diethoxyphosphoryl-1-phenylmethyl)-5-methoxycarbonyl-1,2,3-triazole (3'l)**: Obtained as syrup; R_f (ethyl acetate): 0.33; ^{1}H-nmr, δ_H : 1.15 (m, 6H), 3.87 (s, 3H), 4.05 (m, 4H), 6.36 (d, $^2J_{PH}$ = 21.3 Hz, 1H), 7.34 (m, 5H), 8.74 (s, 1H). ^{13}C-nmr, δ_C : 15.8, 51.6, 60.7 (d, $^1J_{PC}$ = 155.0 Hz), 63.7, 128.7-129.8, 131.71, 139.54, 160.50; ^{31}P-nmr, δ_P : 15.91 ppm; ms, *m/z*: 353 (M^+, 2%); ir, υ: 1732, 1450, 1380, 1310, 1257, 1035 cm^{-1}; Anal. Calcd for $C_{15}H_{20}N_3O_5P$: C, 50.97; H, 5.71; N, 11.90. Found: C, 51.01; H, 5.80; N, 11.97.

1-(1-Diethoxyphosphoryl-1-phenylmethyl)-5-methyl-4-methoxycarbonyl-1,2,3-triazole (3m): Obtained as syrup; R_f (ethyl acetate): 0.32; ^{1}H-nmr, δ_H : 1.20 (m, 6H), 2.43 (s, 3H), 3.90 (s, 3H), 4.21 (m, 4H), 6.88 (d, $^2J_{PH}$ = 22.2 Hz, 1H), 7.28-7.48 (m, 5H); ^{13}C-nmr, δ_C : 12.5, 16.2, 51.8, 60.3 (d, $^1J_{PC}$ = 155.3 Hz), 64.1, 124.4, 148.0, 159.6; ^{31}P-nmr, δ_P : 16.04 ppm; ms, *m/z*: 339 (M^+- N_2, 17%); Anal. Calcd for $C_{16}H_{22}N_3O_5P$: C, 52.30; H, 6.04; N, 11.44. Found: C, 52.32; H, 5.99; N, 11.52. **1-(1-Diethoxyphosphoryl-1-phenylmethyl)-4-methyl-5-methoxycarbonyl-1,2,3-triazole (3'm)**: Obtained as syrup; R_f (ethyl acetate): 0.26; ^{1}H-nmr, δ_H : 1.15 (m, 6H), 2.49 (s, 3H), 3.84 (s,3 H), 4.02 (m, 4H), 5.45 (d, $^2J_{PH}$ = 23.1 Hz, 1H), 7.26-742 (m, 5H); ^{13}C-nmr, δ_C : 8.9, 16.1, 52.2, 59.7 (d, $^1J_{PC}$ = 156.0 Hz), 63.8, 131.8, 139.2, 161.8; ^{31}P-nmr, δ_P : 15.18 ppm; ms, *m/z*: 367 (M^+, 10%); ir, υ: 1720, 1460, 1235, 1018 cm^{-1}; Anal. Calcd for $C_{16}H_{22}N_3O_5P$: C, 52.30; H, 6.04; N, 11.44. Found: C, 52.38; H, 6.08; N, 11.50.

1-(1-Diethoxyphosphoryl-1-phenylmethyl)-4-methoxycarbonyl-5-phenyl-1,2,3-triazole (3n): Obtained as syrup; R_f (ethyl acetate): 0.69; ^{1}H-nmr, δ_H : 1.15 (m, 9H), 4.07 (m, 2H), 4.24 (m, 4H), 6.88 (d, $^2J_{PH}$ = 22.1 Hz, 1H), 7.25-7.68 (m, 10H); ^{13}C-nmr, δ_C : 13.63, 16.2, 61.2 (d, $^1J_{PC}$ = 154.7 Hz), 61.9, 63.5, 124.3, 129.5-132.7, 149.9, 159.0; ^{31}P-nmr, δ_P : 15.88 ppm; ms, *m/z*: 414 (M^+, 47%); Anal. Calcd for $C_{22}H_{26}N_3O_5P$: C, 59.57; H, 5.91; N, 9.48. Found: C, 59.68; H, 5.97; N, 9.52. **1-(1-Diethoxyphosphoryl-1-phenylmethyl)-5-methoxycarbonil-4-phenyl-1,2,3-triazole (3'n)**: Obtained as syrup; Rf (ethyl acetate): 0.54; ^{1}H-nmr, δ_H : 1.13 (m, 9H), 3.97 (m, 2H), 4.24 (m, 4H), 5.52 (d, $^2J_{PH}$ = 22.8 Hz, 1H), 7.33 (m, 10H); ^{13}C-nmr, δ_C : 13.9, 16.1, 60.14 (d, $^1J_{PC}$ = 155.4 Hz), 60.9, 63.9, 125.4, 128.4-130.6, 141.9, 160.6; ^{31}P-nmr, δ_P : 15.21 ppm; ms, *m/z*: 414 (M^+, 37%); ir, υ: 1737, 1450, 1420, 1390, 1263, 1215, 1198 cm^{-1}; Anal. Calcd for $C_{22}H_{26}N_3O_5P$: C, 59.57; H, 5.91; N, 9.48. Found: C, 59.65; H, 6.02; N, 9.54;.

4-Diethoxyphosphoryl-1-(1-diethoxyphosphoryl-1-phenylmethyl)-5-methyl-1,2,3-triazole (3o): Obtained as syrup; R_f (ethyl acetate): 0.27; ^{1}H-nmr, δ_H : 1.03 (m, 12H), 2.29 (s, 3H), 3.92 (m, 4H), 4.04 (m, 4H), 6.59 (d, $^2J_{PH}$ = 22.6 Hz, 1H), 7.38 (m, 5H); ^{13}C-nmr, δ_C : 11.2, 15.8, 60.8 (d, $^1J_{PC}$ = 155.0 Hz), 62.8, 63.7, 122.2 (d,$^1J_{PC}$ = 216.8 Hz), 128.1-132.9, 150.0 (d, $^2J_{PC}$ = 20 Hz); ^{31}P-nmr, δ_P: 16.05, 5.04 ppm; ms, *m/z*: 445 (M^+- N_2, 20%); Anal. Calcd for $C_{18}H_{29}N_3O_6P_2$: C,

48.52; H, 6.56; N, 9.44. Found: C, 48.47; H, 6.52; N, 9.39. **5-Diethoxyphosphoryl-1-(1-diethoxyphosphoryl-1-phenylmethyl)-4-methyl-1,2,3-triazole (3'o)**: Obtained as syrup; R_f (ethyl acetate): 0.11; ^{1}H-nmr, δ_H : *1.22* (m, 12H), *2.40* (s, 3H), 4.21 (m, 8H), 5.68 (d, $^2J_{PH}$ = 23.1 Hz), 7.33 (m, 5H); ^{13}C-nmr, δ_C : 8.5, 16.0, 60.1 (d, $^1J_{PC}$ = 155.4 Hz), 62.7, 63.7, 128.4-131.8, 134.0 (d, $^1J_{PC}$ = 238.6 Hz), 141.2 (d, $^2J_{PC}$ = 28.6 Hz); ^{31}P-nmr, δ_P : 15.87, 8.00 ppm; ms, *m/z*: 445 (M^+, 9%); ir, υ: 1480, 1294, 1260 cm^{-1}; Anal. Calcd for $C_{18}H_{29}N_3O_6P_2$: C, 48.52; H, 6.56; N, 9.44. Found: C, 48.55; H, 6.59; N, 9.50.

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