

Reaction of 2,6-Bis(4-azidobenzylidene)-4-methylcyclohexanone with Organophosphorus Reagents. Synthesis of Some Benzylidene-1, 2, 3-triazole Derivatives

L.S. Boulos* and S.S. Maigali

Organometallic and Organometalloid Chemistry Department ,
National Research Centre, Giza, Egypt.

TRIPHENYLPHOSPHINE (1) reacts with 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone (4) to give the respective triphenylphosphinylidenetriaz-1-enyl (5a) and triphenylphosphinylidene-amino (5b). Moreover, reaction of aryl azide (4) with tris(dimethylamino)phosphine (2) in refluxing toluene afforded the new products (6a, b). On the other hand, phosphorus ylides (3a-d) react with azidobenzylidene (4) to give the corresponding 1,5-disubstituted-1,2,3-triazoles (7a-d) and triphenylphosphine oxide. Possible reaction mechanisms are considered and the structural assignments are based on compatible analytical and spectroscopic results.

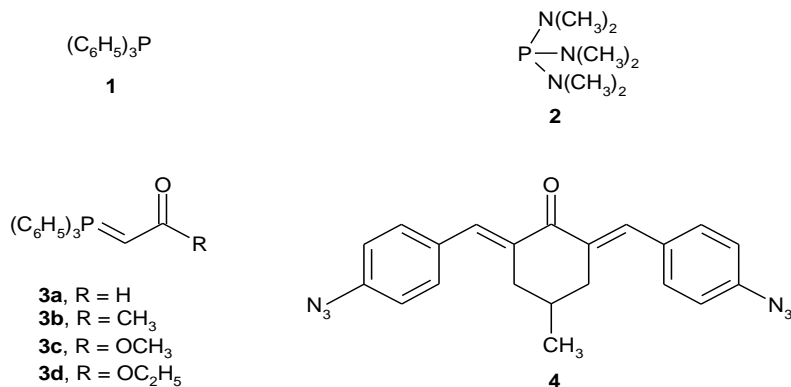
Keywords: 2,6- Bis (4-azidobenzylidene) cyclohexanone, (triphenylphosphinylidenetriaz-1-enyl) benzylidenecyclohex-anone, 1, 2, 3-triazoles and Organophosphorus reagents.

Organic azides are reagents due to their chemical, biological as well as industrial applications⁽¹⁻⁷⁾. Moreover, phosphorus chemistry plays important roles in catalysis^(8,9), polymer science^(10,11), biological engineering⁽¹²⁾, synthetic chemistry⁽¹³⁾, and life⁽¹⁴⁾. It has been reported that organic azides react with organophosphorus reagents to give the corresponding iminophosphoranes^(15, 16). In continuation of our work directed towards study of behavior of organophosphorus reagents towards acid azides^(17,18), the reaction of triphenylphosphine (1), tris(dimethylamino)phosphine (2) and stabilized phosphonium ylides (3a-d) with 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone (4) has been investigated (Scheme 1).

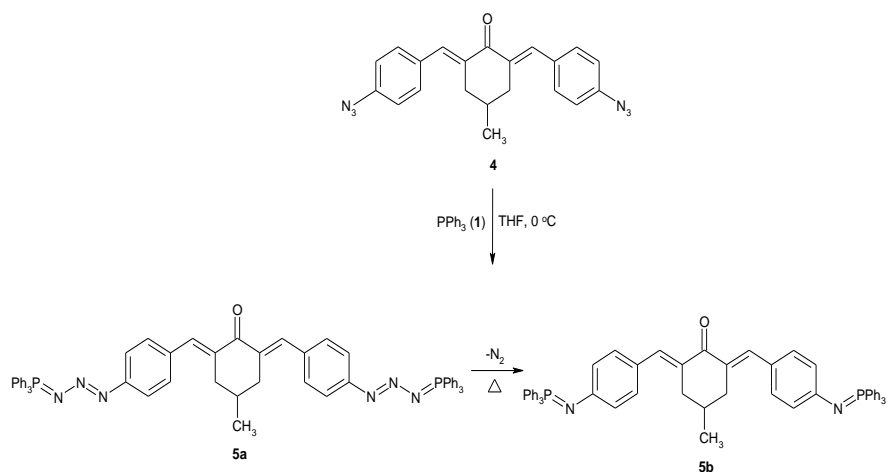
Results and Discussion

2,6-Bis(4-azidobenzylidene)-4-methylcyclohexanone (4) reacts with three mol equivalents of triphenylphosphine (1) in tetrahydrofuran at 0°C to give two products assigned as (5a) (major product) and (5b) (minor product) (Scheme 2).

* E-mail: leilagoubran@yahoo.com



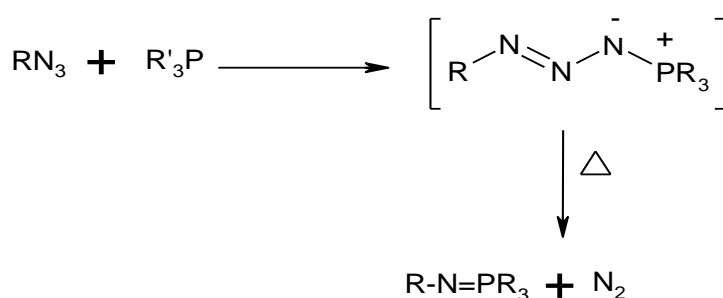
Scheme 1



Scheme 2

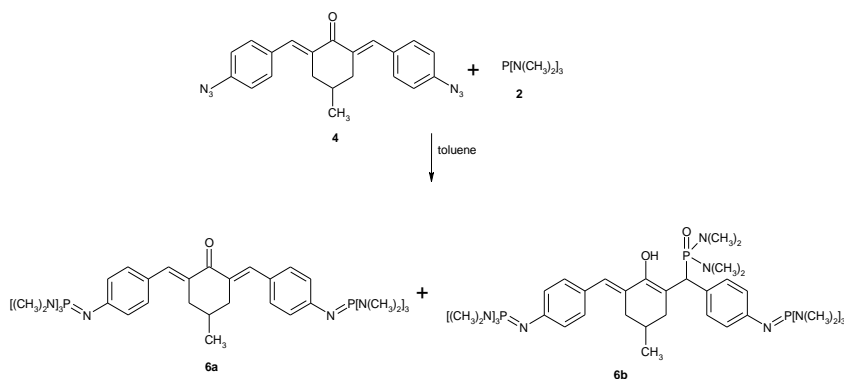
The formed products were purified by column chromatography. Structure elucidation of 4-methyl-2,6-bis[4-(triphenylphosphinylidene)benzylidene]cyclohexanone (5a) is based on the following evidence. Compound 5a exhibits a phosphoranime signal at $\delta = +26.30$ ppm in its ^{31}P NMR spectrum^(17, 19). The IR spectrum reveals the presence of absorption bands at $\nu = 1665$ (C=O), 1433 (P-Ph), 1343 (N=P) cm^{-1} and absence of any azido function group at $\nu = 2100$ cm^{-1} . Elemental analyses data of (5a) supports the molecular formula $C_{57}H_{48}N_6OP_2$. The parent molecular ion peak expected to appear at $m/z = 896$ in the MS spectrum of (5a) was missing. This is attributed to its instability under electron impact (EI-MS) technique. However, bands at $m/z = 277$ (100%), 305 (75%) and 262 (30%) are recognized due to (-HN=PPh₃), (-HN=N=PPh₃) and PPh₃, respectively. The analytical and spectroscopic (IR, 1H -NMR, ^{13}C -NMR and EI-MS) data of compounds 5a and 5b confirm their assigned structure (*c.f.* Experimental section).

It is worthy to mention that, when 2,6-bis(4-azidobenzylidene)-4-methylcyclohexanone (4) allowed to react with three mol equivalents of triphenylphosphine at room temperature in THF, both 5a (minor product) and 5b (major product) are produced. Heating of compound 5a under reduced pressure gives rise to the corresponding iminophosphorane derivative 5b, through loss of nitrogen⁽²⁰⁾ (Scheme 2). Previously, it has been reported^(21, 22) that the reaction of organic azides with triphenylphosphine produces the corresponding iminophosphorane apparently via intermediate phosphine-azide complex which in some cases could be isolated⁽²³⁾ (Scheme 3).



Scheme 3

Furthermore, reaction of azidobenzylidene 4 with tris(dimethylamino) phosphine (2) was also investigated. It has been found that, reaction of tris(dimethylamino) phosphine (2) with azidobenzylidene 4 (as 3:1 molar ratio), in dry toluene proceeds at reflux temperature to give chromatographically pure adducts formulated as 6a and 6b, respectively (Scheme 4).

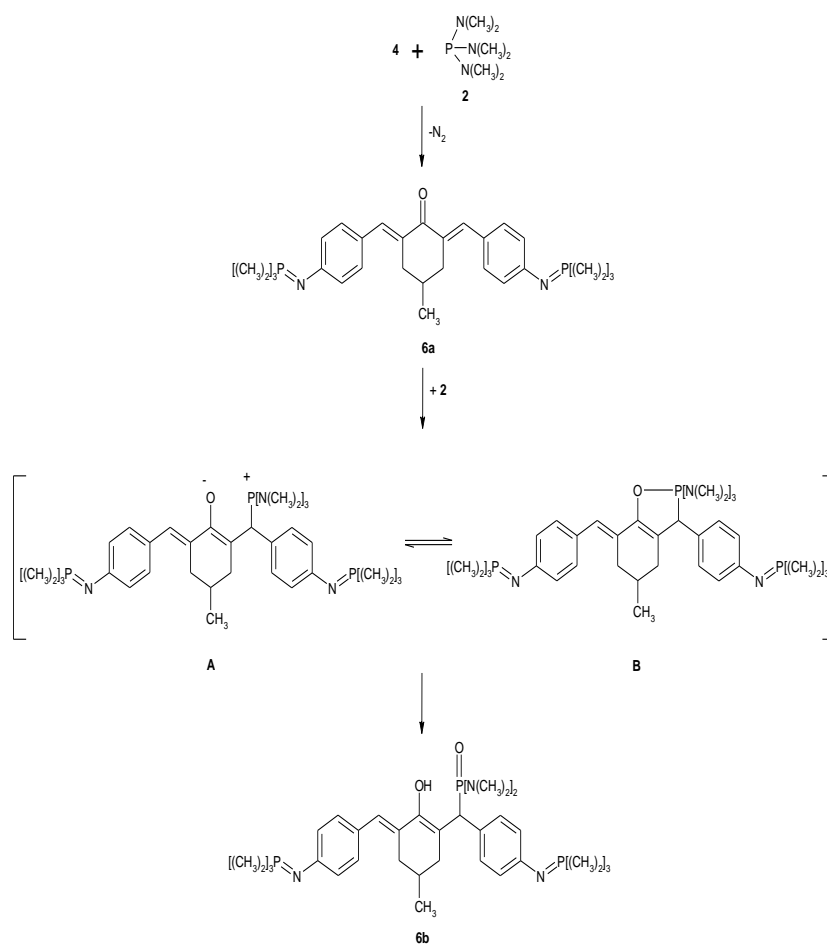


Scheme 4

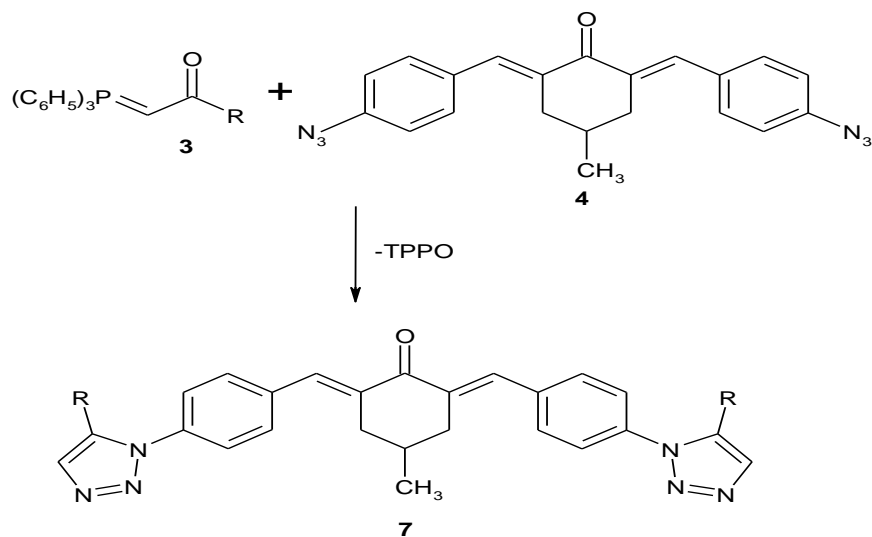
The structures of 6a and 6b were deduced from their elemental analyses as well as IR, ^1H , ^{13}C , ^{31}P NMR and mass spectral data (*c.f.* Experimental section). The reaction presumably, proceeds via addition of tris(dimethylamino)phosphine (2) to the azidobenzylidene (4) giving the iminophosphorane (6a) through loss of nitrogen atoms. The other molecule of tris(dimethylamino) phosphine (2) upon nucleophilic attack of the phosphate-phosphorus on the most reactive center of 6a leads to the dipolar intermediate (A) which undergoes ring closure giving structure (B). The latter, due to its structure features⁽²⁴⁾ could collapse to the most stable form (6b) through rapid hydrolysis of (B) (by the presence of unavoidable moisture) (Scheme 5). Worthy to mention that when one mol equivalent of 6a reacts with one mol equivalent of reagent 2 in refluxing toluene for one hour, 6b is produced in 60% yield (Scheme 5).

The present study has also been extended towards investigation of the reaction of azidobenzylidene (4) with phosphorus ylides (3a-d). It has been noticed that azidobenzylidene (4) reacts with two mol equivalents of formylmethyl-enetriphenylphosphorane (3a) in refluxing toluene giving yellow crystals formulated as 2,6-bis [4-(1*H*-1,2,3-triazol-1-yl) benzylidene] -4-methylcyclo-hexanone (7a). Triphenylphosphine oxide was also isolated from the reaction medium. The structure of 7a was deduced from its IR, ^1H , ^{13}C NMR and mass spectral data together with its correct microanalyses. The IR spectrum of 7a reveals the presence of absorption bands at $\nu = 1665$ (C=O), 1625 (C=C) beside the triazolyl characteristic absorption bands at 1183 and 3100-3140 cm^{-1} (triazole = C-H stretching vibration). Moreover, no absorption bands were observed in the IR spectrum of 7a due to the azido function around 2100 cm^{-1} . ^1H -NMR spectrum of 7a disclosed the presence of signals at $\delta = 1.03$ (d, 3H, CH_3 , $J_{\text{HH}} = 8.1$ Hz), 1.55 (m, 1H, CH), 2.24 (m, 2H, CH_2), 2.29 (m, 2H, CH_2), 7.70 (s, 1H, olefinic H), 7.76 (d, 1H, $J = 5.4$ Hz, CH-N=N), 8.03 (d, 1H, $J = 5.4$ Hz, =CH-N-N). The aromatic protons appear as multiplet signals at $\delta = 7.74$ (8H) ppm. ^{13}C NMR spectrum of 7a shows bands at $\delta = 21.30$ (CH_3), 30.1 (CH_2), 35.67 (CH), 39.32 (CH_2), 123.25 (=CH-N-N), 131.90 (=CH-Ph), 135.39 (=CH-N=N), 136.30 (C-N) and 185.46 (C=O). The mass spectrum of 7a yields a predominant ion peak at $m/z = 422$ (M^+ , 75%). Similarly, phosphorus yields (3b-d) react with azidobenzylidene (4) (as 2:1 molar ratio) to give the corresponding triazole products (7b-d). Triphenylphosphine oxide was also isolated from the reaction mixture (Scheme 6). The structures of 7b-d are deduced from their elemental analyses and spectral data (*c.f.* Experimental section).

A possible explanation of the reaction course of azidobenzylidene (4) with phosphorus ylides (3a-d) is shown in Scheme 7. The reaction can be visualized as 1,3-dipolar cycloaddition of the azide (4) to C=C bond of the ylides (3a-d) (enolate form) occurred in the first step of the reaction followed by loss of OPPh_3 from the cyclic intermediate to give *N*-1 substituted-1,2,3-triazoles (7a-d)^(25, 26). Previously it has been reported that triazoles can be easily obtained through microwave irradiation⁽²⁷⁾.

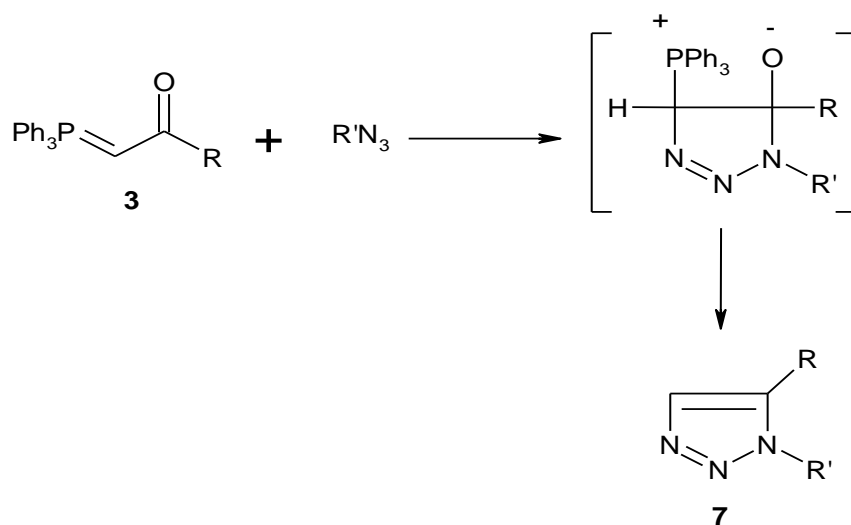


Scheme 5



3a, 7a; R = H
3b, 7b; R = CH₃
3c, 7c; R = OCH₃
3d, 7d; R = OC₂H₅

Scheme 6



Scheme 7

Conclusions

The results of the present investigation allow certain interesting conclusions to be drawn. While azidobenzylidene (**4**) reacts with triphenylphosphine (**1**),

trisdimethylaminophosphine (2) to yield the corresponding iminophosphorane adducts (5a-b) and (6a-b), a different behavior is noted with ylides (3a-d). These ylides give with azidobenzylidene (4), the respective 1,5-disubstituted-1,2,3-triazoles (7a-d). Moreover, it is safe to conclude that the reaction of azidobenzylidene with organophosphorus reagents (1-3) leads to different products depending on the nature of the reagent used as well as the stability of the addition products.

Experimental

Melting points were determined on an Electrothermal digital melting point apparatus and were uncorrected. Elemental analytical data were obtained at the Analytical Laboratory of the National Research Centre. The IR spectra were measured in KBr disks on a JASCO fourier transform infrared Spectrophotometer model FT/IR-3000E. The ^1H NMR spectra were recorded in CDCl_3 and d_6 -DMSO as solvents on JEOL JNM-EX 270 (at 270 MHz) and/or JEOL 500AS (at 500 MHz) Spectrometer using tetramethylsilane (TMS) as an internal reference. ^{13}C NMR spectra were recorded on JEOL 500AS (at 125 MHz). The ^{31}P NMR spectra were taken with a varian CFT-20 (vs. external 85% H_3PO_4 standard). Mass spectra (EI-MS) were determined at 70 eV on a Finnigan MAT S5Q7000 Spectrometer.

Reaction of 2,6-Bis(4-azidobenzylidene)-4-methylcyclohexanone (4) with triphenylphosphine (1)

A solution of azide (4) (0.37 g, 0.001 mol) in dry tetrahydrofuran (30 ml), placed in an ice bath, was added dropwise with shaking a solution of triphenylphosphine (1) (0.79 g, 0.003 mol), so that the temperature did not rise to 0°C . After complete addition, the reaction mixture was cooling then, left at room temperature for 2hr. The reaction mixture was evaporated under reduced pressure. The residue was applied to silica gel column chromatography. The eluent, yield and mp are given below for products 5a and 5b.

4-Methyl-2,6-bis[4-(triphenylphosphinylidenetriaz-1-enyl)benzylidene]cyclohexanone (5a)

Eluent: acetone/petroleum ether (30:70 v/v), yellow crystals, m.p. $55\text{--}56^\circ\text{C}$, yield 70%. Anal. Calcd. for $\text{C}_{57}\text{H}_{48}\text{N}_6\text{OP}_2$ (894): C, 76.51; H, 5.36; N, 9.39; P, 6.93. Found: C, 76.35; H, 5.12; N, 9.30; P, 6.55. IR: $\nu = 1665$ (C=O), 1433 (P-phenyl), 1343 (P=N). ^1H NMR: $\delta = 0.96$ (d, 3H, CH_3 , $J_{\text{HH}} = 8.1$ Hz), 2.09 (m, 1H, CH, $J_{\text{HH}} = 5.4$ Hz), 2.90 (m, 2H, CH_2 , $J_{\text{HH}} = 5.2$ Hz), 2.93 (s, 2H, CH_2 , $J_{\text{HH}} = 5.2$ Hz), 6.59 (s, 2H, =CHPh), 7.35-7.38 (m, 8H, arom. H), 7.41-7.59 (m, 30 H, arom. H). ^{13}C NMR: $\delta = 22.57$ (CH_3), 36.57 (CH_2), 37.15 (CH), 50.69 (CH_2), 132.26 (=CH-Ph), 188.25 (C=O). ^{31}P NMR: $\delta = 26.30$.

4-Methyl-2,6-bis[4-(triphenylphosphinylideneamino)benzylidene]cyclohexanone (5b)

Eluent: acetone/petroleum ether (50:50 v/v), deep yellow crystals, m.p. 240°C , yield 15%. Anal. Calcd. for $\text{C}_{57}\text{H}_{48}\text{N}_2\text{OP}_2$ (838): C, 81.62; H, 5.72; N, 3.34; P, 7.39. Found: C, 81.50; H, 5.42; N, 3.21; P, 7.22. IR: $\nu = 1704$ (C=O),

1436 (P-phenyl), 1340 (P=N). ^1H NMR: $\delta = 1.02$ (d, 3H, CH_3 , $J_{\text{HH}} = 8.1$ Hz), 2.08 (m, 1H, CH, $J_{\text{HH}} = 5.0$ Hz), 2.43 (m, 2H, CH_2 , $J_{\text{HH}} = 4.5$ Hz), 2.91 (m, 2H, CH_2 , $J_{\text{HH}} = 4.5$ Hz), 5.64 (s, 2H, =CHPh), 6.41-6.58 (m, 8H, arom. H), 7.23-7.58 (m, 30 H, arom. H). ^{13}C NMR: $\delta = 22.12$ (CH_3), 39.51 (CH), 40.01 (CH_2)₂, 123.51 (C-N), 133.00 (=CH-Ph), 188.42 (C=O). ^{31}P NMR: $\delta = 20.43$. MS: m/z (%) 837 [($\text{M}^+ - 1$), 10], 561 [($\text{M}^+ - (\text{N-PPH}_3)$), 70], 285 [($\text{M}^+ - 2 (\text{N-PPH}_3)$), 95].

Applying the same reaction at room temperature, a solution of arylazide 4 (0.001 mol) was added to a solution of 1 (0.002 mol) in dry THF, and left at room temperature during which nitrogen gas was evolved. The same adducts 5a (15%) and 5b (80%) were isolated.

Action of heat on phosphorus triazo adduct (5a)

Adduct 5a (0.2 g) was heated in cold finger sublimation at 120°C (bath temperature under reduced pressure (2 mm/Hg) for 10 min. The substance that sublimed was cooled, crystallized from acetone- petroleum ether (60-80°C) to give iminophosphorane derivative 5b in 85% yield, m.p. 240 °C (mixed m.p. and comparative IR spectra).

Reaction of azidobenzylidene (4) with tris (dimethylamino) phosphine (2)

A mixture of azide 4 (0.37g, 0.001 mol) and reagent 2 (0.49 g, 0.003 mol) in dry toluene (30 ml) was refluxed for 1 hr. The solvent was evaporated under reduced pressure, the residue was chromatographed on a silica gel column chromatography to give two products formulated as 6a (minor product) and 6b (major product).

Compound 6a: Eluent: pet.ether (60-80°C)/acetone (60:40 v/v) product 6a was isolated as yellow crystals, m.p. 65°C, Anal. Calcd. for $\text{C}_{33}\text{H}_{54}\text{N}_8\text{OP}_2$ (640): C, 61.85; H, 8.49; N, 17.49; P, 9.67. Found: C, 61.73; H, 8.15; N, 17.32; P, 9.51. IR: $\nu = 1668$ (C=O), 1325, 835 [P-N(CH_3)₂]. ^1H NMR: $\delta = 0.93$ (d, 3H, CH_3 , $J_{\text{HH}} = 8.1$ Hz), 1.67 (m, 1H, CH, $J_{\text{HH}} = 4.1$ Hz), 1.76-2.24 (m, 4H, 2 CH_2 , $J_{\text{HH}} = 8.1$ Hz), 2.24 {d, 36H, 2 P[N(CH_3)₂]₃, $^3J_{\text{HP}} = 5.1$ Hz} , 7.34 (s, 2H, =CHPh), 7.39-7.69 (m, 8H, arom. H). ^{13}C NMR: $\delta = 22.80$ (CH_3), 34.52 [N(CH_3)₂]₃, 36.5 (2 CH_2), 38.31 (CH), 132.12 (=CH-Ph), 152.54 (C-N=P), 187.52 (C=O) . ^{31}P NMR: $\delta = 22.51$. MS: m/z (%) 640 (M^+ , 8), 461 [($\text{M}^+ - \text{N}=\text{P}[\text{N}(\text{CH}_3)_2]_3$), 99].

Compound 6b: Eluent: pet. ether (60-80 °C)/acetone (70:30 v/v) product 6b was isolated as deep yellow crystals, m.p. 310°C, Anal. Calcd. for $\text{C}_{39}\text{H}_{73}\text{N}_{11}\text{O}_2\text{P}_3$ (820): C, 57.07; H, 8.90; N, 18.78; P, 11.71. Found: C, 57.01; H, 8.52; N, 18.63; P, 11.52. IR: $\nu = 3409$ (OH), 1398 (N=P), 1320, 838 {P[N(CH_3)₂]₃}, 1230 (P=O) . ^1H NMR: $\delta = 0.82$ (d, 3H, CH_3 , $J_{\text{HH}} = 10$ Hz), 1.28 (m, 1H, CH, $J_{\text{HH}} = 4.1$ Hz), 2.04 (m, 4H, 2 CH_2), 2.49, 2.59 {2d, 36H, 12 H, 2 P[N(CH_3)₂]₈}, 4.10 (d, 1H, CH-P, $^2J_{\text{HP}} = 10$ Hz), 6.65 (s, 1H, =CHPh), 7.46-7.66 (m, 8H, arom. H), 9.98 (OH, exchangeable with D_2O). ^{13}C NMR: $\delta = 22.64$ (CH_3), 33.70 (2 CH_2), 36.94 (CH), 37.35, 38.61 {2d, P[N(CH_3)₂]₃}, 40.32 {d,

$\text{O}=\text{P}[\text{N}(\text{CH}_3)_2]_2$, 51.01 (d, CH-P, $^1J_{\text{CP}} = 107$ Hz), 131.89 (s, =CH-Ph), 165.19(C=O). ^{31}P NMR: $\delta = 35.44$ $[(\text{H}_3\text{C})_2\text{N}]_2(\text{P}=\text{O})$, 24.29 $\{\text{P}[\text{N}(\text{CH}_3)_2]_3\}$. MS: m/z (%) 820 (M^+), 633 $\{[(\text{M}^+ - \text{N}=\text{P}[\text{N}(\text{CH}_3)_2]_3), 75\}$, 526 $\{\text{M}^+ - \text{O}=\text{P}[\text{N}(\text{CH}_3)_2]_2, 95\}$.

Reaction of compound 6a with trisaminophosphine (2)

When compound 6a was added to reagent 2 (1:1 molar ratio) in dry refluxing toluene for 1hr. The solvent evaporated under reduced pressure, the residue was purified by a silica gel column chromatography eluting with benzene/ethyl acetate (80:20, v/v) to give compound 6b, 60% yield (m.p., mixed m.p.=65°C).

Reaction of azidobenzylidene(4) with formylmethylenetriphenylphosphorane (3a)

To a solution of 4 (0.37 g, 0.001 mol) in dry toluene (30 ml) was added 3a (0.10 g, 0.001 mol). The reaction mixture was refluxed for 1 hr. When no more of the material was detected (TLC), the mixture was evaporated under reduced pressure. The residue was placed on a column of silica gel and eluent solution to give adduct 7a along with triphenylphosphine oxide (m.p. and mixed m.p.).

2,6-Bis[4-(1H-1,2,3-triazol-1-yl)benzylidene]-4-methylcyclohexanone (7a)

Eluent: pet. ether (60-80°C)/acetone (60:40 v/v) product 7a was isolated as yellow crystals, m.p. 320°C, yield 65%, Anal. Calcd. for $\text{C}_{25}\text{H}_{22}\text{N}_6\text{O}$ (422): C, 71.09; H, 5.21; N, 19.90. Found: C, 71.00; H, 5.10; N, 19.52. IR: $\nu = 3140$ -3100 (triazolyl CH), 1665 (C=O), 1625 (C=C), 1120-950 (triazole nucleus). ^1H NMR: $\delta = 1.03$ (d, 3H, CH_3 , $J_{\text{HH}} = 8.1$ Hz), 1.55 (m, 1H, CH), 2.24 (m, 2H, CH_2), 2.29 (m, 2H CH_2), 7.70 (s, 2H, =CHPh), 7.76 (d, 2H, $J_{\text{HH}} = 5.4$ Hz, CH-N=N), 8.03 (d, 1H, $J_{\text{HH}} = 5.4$ Hz, =CH-N-N), 7.70-7.79 (m, 8H, arom. H). ^{13}C NMR: $\delta = 21.30$ (CH_3), 35.67 (CH), 39.32 (CH_2), 123.25 (=CH-N-N), 131.90 (=CH-Ph), 135.39 (CH-N=N), 136.30 (C-N), 188.46(C=O). MS: m/z (%) 422 (M^+ , 60).

Reaction of 4 with acetylmethylenetriphenylphosphorane (3b)

A mixture of 4 (0.37 g, 0.001 mol) and 3b (0.32 g, 0.001 mol) in dry toluene (30 ml) was refluxed for ½ hr. When no more starting material was detected (TLC), the mixture was evaporated under reduced pressure. The residue was placed on column of silica gel and using eluent solution to give adduct 7b together with triphenylphosphine oxide.

4-Methyl-2,6-bis[4-(5-methyl-1H-1,2,3-triazol-1-yl)benzylidene]cyclohexanone (7b)

Eluent: pet. ether (60-80 °C)/acetone (20:80 v/v) product 7b was isolated as yellow crystals, m.p. 202 °C, yield 62%, Anal. Calcd. for $\text{C}_{27}\text{H}_{26}\text{N}_6\text{O}$ (450): C, 72.00; H, 5.77; N, 18.66. Found: C, 71.97; H, 5.55; N, 18.30. IR: $\nu = 1662$ (C=O), 1604, 1510 (C=C), 1183 (triazole nucleus). ^1H NMR: $\delta = 1.05$ (d, 3H, CH_3 , $J_{\text{HH}} = 9$ Hz), 1.53 (m, 1H, CH), 1.89 (m, 2H, CH_2), 2.39 (m, 2H CH_2), 2.51 (d, 3H, CH_3), 7.74 (m, 1H, C=CH-PhN), 7.81 (q, 1H, =CH-N=N), 7.32-7.51 (m, 8H, arom. H). ^{13}C NMR: $\delta = 8.92$ (CH_3), 21.18 (CH- CH_3), 35.69 (CH- CH_3),

38.66 (CH₂), 40.33 (CH₂), 131.38 (=CH-Ph), 133.20 (CH-N=N), 134.30 (C-N), 136.57 (CH₃-C-N), 185.5(C=O). MS: *m/z* (%) 450 (M⁺, 85).

Similarly, azide (4) reacted with methoxycarbonylmethylenetriphenylphosphorane (3c) to give 2,6-bis [4-(5-methoxy-1*H*-1,2,3- triazol-1-yl) benzylidene] -4-methylcyclohexanone (7c). Eluent: pet. ether (60-80 °C)/ethyl acetate (15:85 v/v) product 7c was isolated as yellow crystals, m.p. 244 °C, yield 65%, Anal. Calcd. for C₂₇H₂₆N₆O₃ (482): C, 67.21; H, 5.39; N, 17.42. Found: C, 67.12; H, 5.22; N, 17.30. IR: ν = 3100-3140 (triazolyl CH), 1663 (C=O), 1653, 1520 (C=C), 1185 (triazole nucleus). ¹H NMR: δ = 0.97 (d, 3H, CH₃, *J*_{HH} = 9 Hz), 1.37 (m, 1H, CH), 1.99 (m, 2H, CH₂), 2.17 (m, 2H CH₂), 3.08 (s, 3H, OCH₃), 7.36 (s, 1H, =CHPh), 7.9 (s, 1H, CH-N=N), 7.63-7.76 (m, 8H, arom. H). ¹³C NMR: δ = 21.60 (CH₃), 35.52 (CH), 36.54 (CH₂), 38.52 (CH₂), 50.31 (OCH₃), 114.31 (=CH-N=N), 131.87 (OC=CH), 132.83 (=CH-Ph), 136.34 (C-N), 188.53 (C=O). MS: *m/z* (%) 480 [(M⁺ - 2), 70].

The ethoxytriazol (7d) was similarly obtained through reaction of 4 (0.37 g, 0.001 mol) and ethoxycarbonylmethylenetriphenylphosphorane (3d) (0.35 g, 0.001 mol) in dry toluene (30 ml) and refluxed for ½ hr. The solvent was distilled off and the residue was placed on a column of silica gel using pet. ether (60-80 °C)/ethyl acetate as eluent (80:20 v/v) to product 2,6-bis[4-(5-methoxy-1*H*-1,2,3-triazol-1-yl)benzylidene]-4-methylcyclohexanone (7d) as orange crystals, m.p. 245 °C, yield 66%, Anal. Calcd. for C₂₉H₃₀N₆O₃ (510): C, 68.23; H, 5.88; N, 16.47. Found: C, 68.12; H, 5.53; N, 16.25. ¹H NMR: δ = 0.98 (d, 3H, CH₃, *J*_{HH} = 9 Hz), 1.32 (t, 3H, CH₃CH₂), 1.53 (m, 1H, CH), 1.68 (m, 2H, CH₂), 2.05 (m, 2H, CH₂), 4.21 (q, 2H, CH₂CH₃), 6.98 (s, 1H, CH-Ph), 7.82 (s, 1H, CH-N=N), 7.38-7.52 (m, 8H, arom. H). MS: *m/z* (%) 510 (M⁺, 60).

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**تفاعل 2، 6- ثنائى (4- أزيدوبنزيليدين)-4- ميثيل
هكسانون الحلقي مع الكواشف العضوية الفوسفورية .
تشبيد بعض مشتقات البنزيليدين-1،2،3- ترايازول**

ليلى صادق بولس و سهير سعيد مجلى
قسم كيمياء عضوية فلزية وعضوية شبة فلزية - المركز القومى
للبحوث - الجيزة - مصر .

نظرا لأهمية مركبات الأزيد العضوية فى التطبيقات الكيميائية والبيولوجية والصناعية بالإضافة الى أهمية كيمياء الفوسفور ودورها فى تحضير مركبات تستخدم كعوامل حفازة فى التفاعلات الكيميائية والهندسة البيولوجية و الكيمياء التشبيدية.

لذا تم دراسة سلوك الكواشف العضوية الفوسفورية المختلفة تجاه مركب الأزيد. فعند تفاعل مركب الأزيدوبنزيليدين مع ثلاثى فينيل الفوسفين عند درجة حرارة الصفر المئوى تم الحصول على مركب ثلاثى فينيل فوسفنيليدين ترى أزانيل (نتج رئيسى) ، بالإضافة الى مركب ثلاثى فينيل فوسفنيليدين (نتج ثانوى).

وعند اجراء نفس التفاعل فى درجة حرارة الغرفة تم الحصول على المركبين السالف ذكرهما بنسب مئوية مختلفة. ولقد تم الحصول على مركبين جديدين عند تفاعل الأزيدوبنزيليدين مع ثلاثى (ثنائى ميثيل أمينو)- فوسفين فى مذيب الطولين مع التسخين و قد أمتدت الدراسة لتشمل تفاعل الأزيدوبنزيليدين مع أيليدات الفوسفور ليعطى مشتقات الترايازول على الترتيب بالإضافة الى مركب أكسيد ثلاثى فينيل الفوسفين.

ميكانيكية التفاعلات والتركيبات البنائية للمركبات الجديدة المشيدة تم دراستها ومناقشتها بناء على النتائج التحليلية والطيفية مثل الأشعة تحت الحمراء والرنين النووى المغناطسى لنواة ذرة كل من الهيدروجين والكربون والفوسفور وطيف الكتلة وأيضا الكتلة وأيضا التحليل الكمى للعناصر.

