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Allenephosphonic phosphine oxides in reactions with electrophilic reagents

D. D. Enchev
Department of Chemistry, Faculty of Natural Sciences, "Konstantin Preslavsky" University,
Universiteska 115, 9712, Shumen, Bulgaria
e mail: d.enchev@shu.bg

Abstract: *The reactivity of the titled compounds towards electrophilic reagents has been investigated and new experimental evidences for the mechanism of the electrophilic addition reactions to 1,2-alkadienephosphonates have been reported*

Keywords: *electrophilic addition, nucleophilic addition, 1,2-alkadienephosphonates*

Introduction

It is well documented that electrophilic addition reactions to 1,2-alkadienephosphonates lead to 2,5-dihydro-1,2-oxaphosphole-2-oxide derivatives. [1] The mechanism of this reaction involves the formation of carbocation specie, which is in equilibrium with quasiphosphonium intermediate. The latest undergo a Michaelis-Arbuzov reaction (second stage) to the final oxaphosphole derivatives.
The formation of the above mentioned quasiphosphonium intermediate is critical for the final oxaphosphole derivative isolation. [2] The characterization of this intermediate is difficult tack because of the rapid dealkylation of it. These difficulties require special design of the structure of the substrate, i.e. prevention of the final dealkylation. One of the suitable substrates for such a strategy are the 1,2-alkadienephosphonic dichlorides. Unfortunately the formatting quasiphosphonium intermediates in these reactions with the mentioned substrates are very unstable which prevent their characterization. [3]
Using by this reaction of allene-substituted tertiary phosphine oxides is more promising approach.

Results and Discussion

Here we wish to report our results from the investigation of the scope of electrophilic addition reaction to above mentioned substrates. The latest were synthesized by the reaction of

Corresponding author: d.enchev@shu.bg
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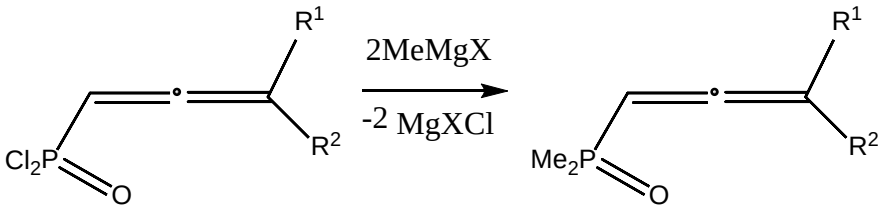
dichlorides of 1,2-alkadienephosphonic acids with Grinjard reagents generated in situ. [4] The reaction followed the scheme:



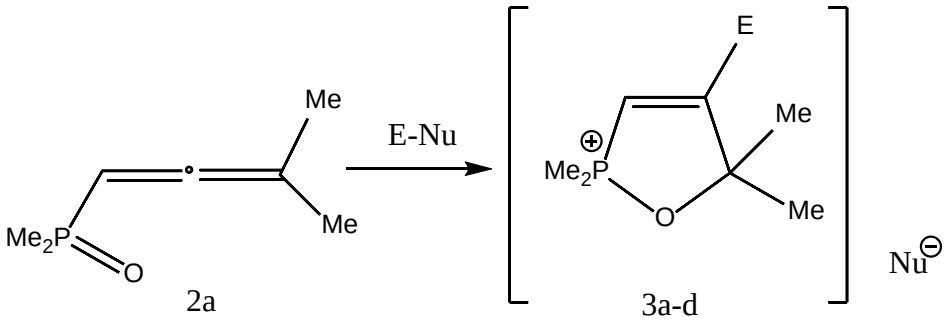
1 2a,b

R^1=R^2=Me; R^1=H, R^2=Pr

2a. $C_7H_{13}OP$; m.p. (°C) uncorrected 120-122, 0.34 g (47%); Calcd.: P 21.48 %, Found: P 21.41 %; IR(KBr) νmax/cm-1 1945 (C=C=C), 1225 (P=O), 1H NMR (80MHz, $CDCl_3$), δ/ppm : 5.73 [m; $^2J_{HP}$ 6.8 Hz, $^4J_{HH}$ 3.4 Hz, 1H, (HC=)]; 0.90 [ss, 6H, (=C(CH_3)$_2$]; 2.18 [ss, 6H, (P(CH_3)$_2$];

2b. $C_8H_{15}OP$; m.p. (°C) uncorrected 122-124, 0.35 g (45%); Calcd.: P 19.58 %, Found: P 19.44 %; IR(KBr) νmax/cm-1 1945 (C=C=C), 1225 (P=O), ^{1}H NMR (80MHz, $CDCl_3$), δ/ppm : 5.34 [m; $^2J_{HP}$ 6.8 Hz, $^4J_{HH}$ 3.4 Hz, 1H, (HC=)]; 2.04 [m; $^4J_{HH}$ 3.4 Hz, 1H (=CH)];1.58 [m; 2H ($CH_2CH_2CH_3$)]; 1.44 [m; 2H ($CH_2CH_2CH_3$)]; 0.92 [m; 9H, (CH_3)$_2$P), ($CH_2CH_2CH_3$)];

The synthesized by us allenephosphine oxides were studied in reaction with some electrophilic reagents [5]:



2a 3a-d

E-Nu = Br_2, I_2, MeSCl, MeSeCl

3a. $C_7H_{13}Br_2OP$; powder, 1.32 g (87%); Calcd.: P 10.19, Br 52.57 %, Found: P 9.98, Br 52.36 %; IR(KBr) νmax/cm-1 1550 (C=C), 950 (P-O-C), ^{1}H NMR (80MHz, CDCl3), δ/ppm : 6.35 [d, $^2J_{HP}$ 36.6 Hz, 1H, (HC=)];1.34 [s, 6H, (2X=CCH_3)]; 1.86 [d, $^2J_{HP}$ 15.6 Hz 6H, (2X PCH_3)]; ^{31}P 107.1;

Corresponding author: d.enchev@shu.bg

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3b. $C_7H_{13}I_2OP$; powder, 1.71 g (86%); Calcd.: P 7.78 %, Found: P 7.54 %; IR(KBr) νmax/cm-1 1545 (C=C), 990 (P-O-C), ^{1}H NMR (80MHz, $CDCl_3$), δ/ppm : 6.48 [d, $^2J_{HP}$ 32.4 Hz, 1H, (HC=)];1.38 [s, 6H, (2X=CCH_3)]; 1.92 [d, $^2J_{HP}$ 15.4 Hz 6H, (2X PCH_3)]; ^{31}P 107.7;
3c. $C_8H_{16}ClOPS$; powder, 0.97 g (86%); Calcd.: P 13.66, Cl 15.63, S 14.14 %, Found: P 13.12, Cl 15.35, S 13.98 %; IR(KBr) νmax/cm-1 1520 (C=C), 980 (P-O-C), ^{1}H NMR (80MHz, $CDCl_3$), δ/ppm : 6.50 [d, $^2J_{HP}$ 31.2 Hz, 1H, (HC=)];1.60 [s, 6H, (2X=CCH_3)]; 2.44 [d, $^2J_{HP}$ 15.6 Hz 6H, (2X PCH_3)]; 2.54 [s; 3H (SCH_3)]; ^{31}P 107.7
3d. $C_8H_{16}ClOPSe$; powder, 1.71 g (86%); Calcd.: P 11.31, Cl 12.95 %, Found: P 10.99, Cl 12.74%; IR(KBr) νmax/cm-1 1575 (C=C), 990 (P-O-C), ^{1}H NMR (80MHz, $CDCl_3$), δ/ppm : 6.22 [d, $^2J_{HP}$ 36.0 Hz, 1H, (HC=)];1.72 [s, 6H, (2X=CCH_3)]; 2.42 [d, $^2J_{HP}$ 15.8 Hz 6H, (2X PCH_3)]; 2.16 [s; 3H (SeCH_3)]; ^{31}P 107.7

The interaction of dimethyl(3-methyl-1,2-butadienyl)phosphine oxide with electrophilic reagents leads to obtaining of the cyclic phosphonium salts **3a-d**. These compounds are powders, resistible on air, with good water solubility and other polar solvents and practically insoluble in organic solvents. The chemical shifts for ^{31}P in the ^{31}P NMR spectra of these compounds are very characteristic and confirm the phosphonium structure of the compounds obtained. The isolation of the above mentioned compounds is indirect, but good enough evidence supporting the suggested mechanism of the reaction. The discussed reaction mechanism involves initial formation of tertiary carbonium ion, easily transformable to cyclic phosphonium specie, stabilized by the anion. An additional evidence for the above statement is the fact that the chlorination of dimethyl(1,2-hexadienyl)phosphine oxide, which involves the formation of a secondary carbonium ion, but not the tertiary ones, leads to isolation of 2,3-adducts(E/Z-isomeric mixture) and their 1,3-sigmatropic rearrangement products, while the oxaphosphonium salt is only 10% from the total yield of the reaction:[5]

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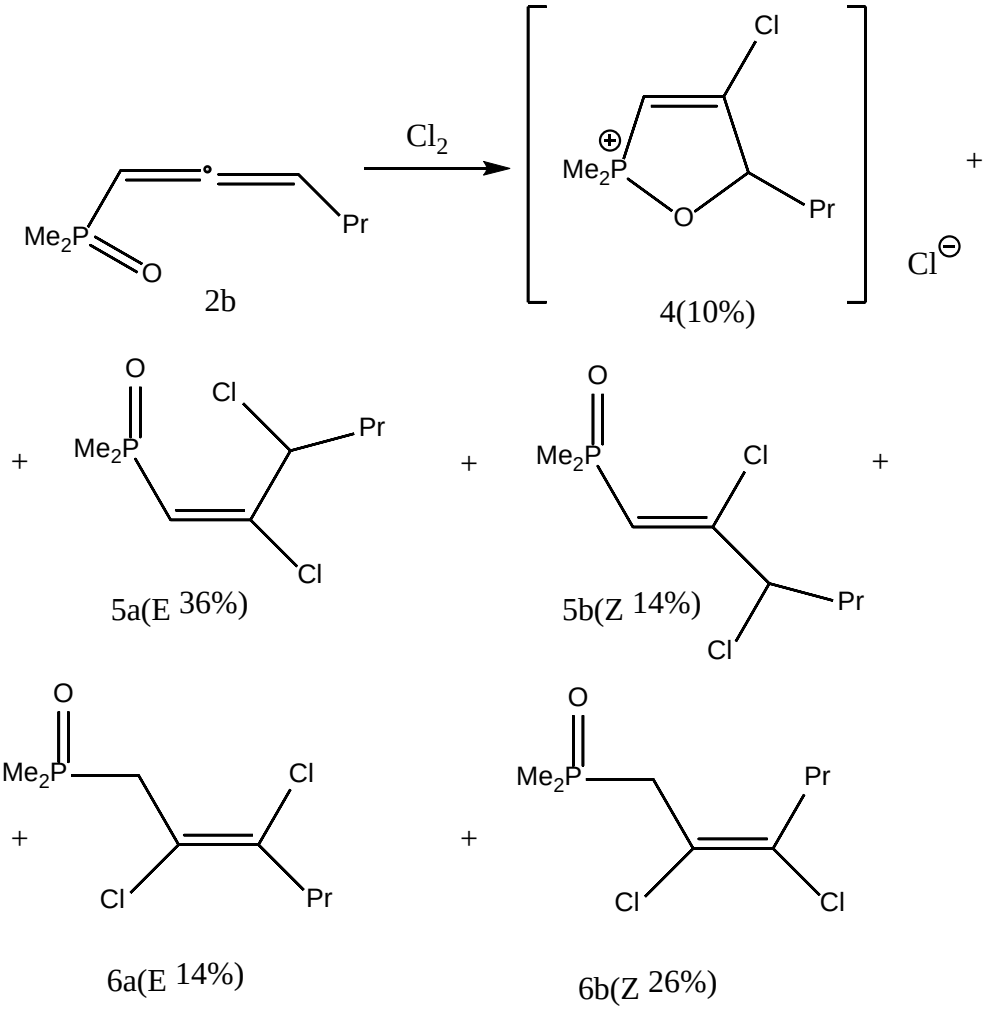

4. ^{1}H NMR (80MHz, $CDCl_3$), δ/ppm : 7.25 [d, $^{2}J_{HP}$ 29.0 Hz, 1H, (HC=)]; 1.34 [s, 6H, (2X=CCH_3)]; 1.86 [d, $^{2}J_{HP}$ 15.6 Hz 6H, (2X PCH_3)];
5a. ^{1}H NMR (80MHz, $CDCl_3$), δ/ppm : 5.93 [dd, $^{2}J_{HP}$ 13.2 Hz, 1H, (HC=)]; 4.46 [m; 1H (=CH)]; 0.93 [m, 9H, ($CH_2CH_2CH_3$),(2X PCH_3)]; 1.33 [m; 2H ($CH_2CH_2CH_3$)]; 1.57 [m; 2H ($CH_2CH_2CH_3$)];
5b. ^{1}H NMR (80MHz, $CDCl_3$), δ/ppm: 6.38 [d, $^{2}J_{HP}$ 11.2 Hz, 1H, (HC=)]; 5.28 [m; 1H (=CH)]; 0.93 [m, 9H, ($CH_2CH_2CH_3$), (2X PCH_3)]; 1.33 [m; 2H ($CH_2CH_2CH_3$)]; 1.57 [m; 2H ($CH_2CH_2CH_3$)];
6a. ^{1}H NMR (80MHz, $CDCl_3$), δ/ppm: 3.34 [d, $^{2}J_{HP}$ 16.0 Hz, 2H, (H_2CC=)]; 0.93 [m, 9H, ($CH_2CH_2CH_3$), (2X PCH_3)]; 1.44 [m; 2H ($CH_2CH_2CH_3$)]; 1.96 [m; 2H ($CH_2CH_2CH_3$)];
6b. ^{1}H NMR (80MHz, $CDCl_3$), δ/ppm: 2.32 [d, $^{2}J_{HP}$ 14.4 Hz, 2H, (H_2CC=)]; 0.93 [m, 9H, ($CH_2CH_2CH_3$), (2X PCH_3)]; 1.44 [m; 2H ($CH_2CH_2CH_3$)]; 1.96 [m; 2H ($CH_2CH_2CH_3$)];

By the reaction of the titled compounds with phenylsulphenyl- and phenylselenenylbromides a compounds with phosphonium structure are isolated. The typical chemical shifts for ^{31}P in their ^{31}P NMR spectra i.e.105-110ppm is an evidence for that, as well as, the other properties, namely solubility in inorganic polar solvents and insolubility in

Corresponding author: d.enchev@shu.bg
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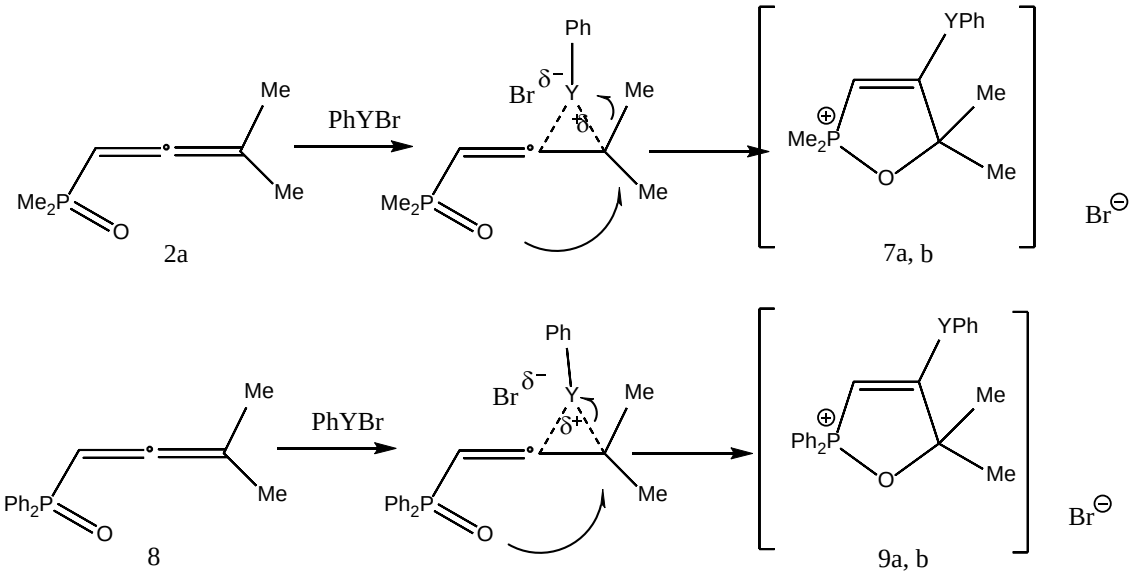
organic ones. The reaction mechanism involved the formation of episulphonium/ episelenunium species, which undergo an intramolecular nucleophilic attack from the phosphryl group oxygen atom to formation of the end products:[6]



Y = S, Se

7a. $C_{13}H_{18}BrOPS$; powder, 0.97 g (86%); Calcd.: P 8.34, Br 21.52, S, 8.63 %, Found: P 8.22, Br 21.35, S 8.51 %; IR(KBr) νmax/cm-1 1520 (C=C), 980 (P-O-C), ^{1}H NMR (100MHz, CDCl3), δ/ppm : 7.56-7.23 (m, 5H, Ph), 6.50 [d, $^{2}J_{HP}$ 31.2 Hz, 1H, (HC=)];1.60 [s, 6H, (2X=CCH_3)]; 2.44 [d, $^{2}J_{HP}$ 15.6 Hz 6H, (2X PCH_3)]; ^{3}1P NMR (H_3PO_4): 107.7

7b. $C_{13}H_{18}BrOPSe$; powder, 1.71 g (86%); Calcd.: P 7.40, Br 19.11 %, Found: P 7.12, Br 19.09%; IR(KBr) νmax/cm-1 1575 (C=C), 990 (P-O-C), ^{1}H NMR (100MHz, CDCl3), δ/ppm : 7.56-7.23 (m, 5H, Ph), 6.22 [d, $^{2}J_{HP}$ 36.0 Hz, 1H, (HC=)];1.72 [s, 6H, (2X=CCH_3)]; 2.42 [d, $^{2}J_{HP}$ 15.8 Hz 6H, (2X PCH_3); ^{31}P NMR (H_3PO_4): 101.7

9a, $C_{23}H_{22}BrOPS$; powder, 0.97 g (86%); Calcd.: P 6.67, Br 17.47, S 7.01 %, Found: P 6.22, Br 17.35, S 6.91 %; IR(KBr) νmax/cm-1 1520 (C=C), 980 (P-O-C), ^{1}H NMR (100MHz, CDCl3), δ/ppm : 7.56-7.23 (m, 5H, Ph),7.45-7.33 (mm, 10H 2XPh); 5.50 [d, $^{2}J_{HP}$ 31.2 Hz, 1H, (HC=)];1.60 [s, 6H, (2X=CCH_3)]; ^{31}P NMR (H_3PO_4): 110.1

9b, $C_{23}H_{22}BrOPSe$; powder, 0.91 g (82%); Calcd.: P 6.14, Br 15.8 %, Found: P 6.02, Br 15.35 %; IR(KBr) νmax/cm-1 1520 (C=C), 980 (P-O-C), ^{1}H NMR (100MHz, $CDCl_3$), δ/ppm : 7.56-7.23 (m, 5H, Ph),7.45-7.33 (mm, 10H 2XPh); 5.50 [d, $^{2}J_{HP}$ 31.2 Hz, 1H, (HC=)];1.60 [s, 6H, (2X=CCH_3)]; ^{31}P NMR (H_3PO_4): 110.1

Additional evidence is the preparative isolation of the compounds 85a-c by the reaction of the titled compounds with dialkoxyphosphorylsulphenyl chlorides: [7]

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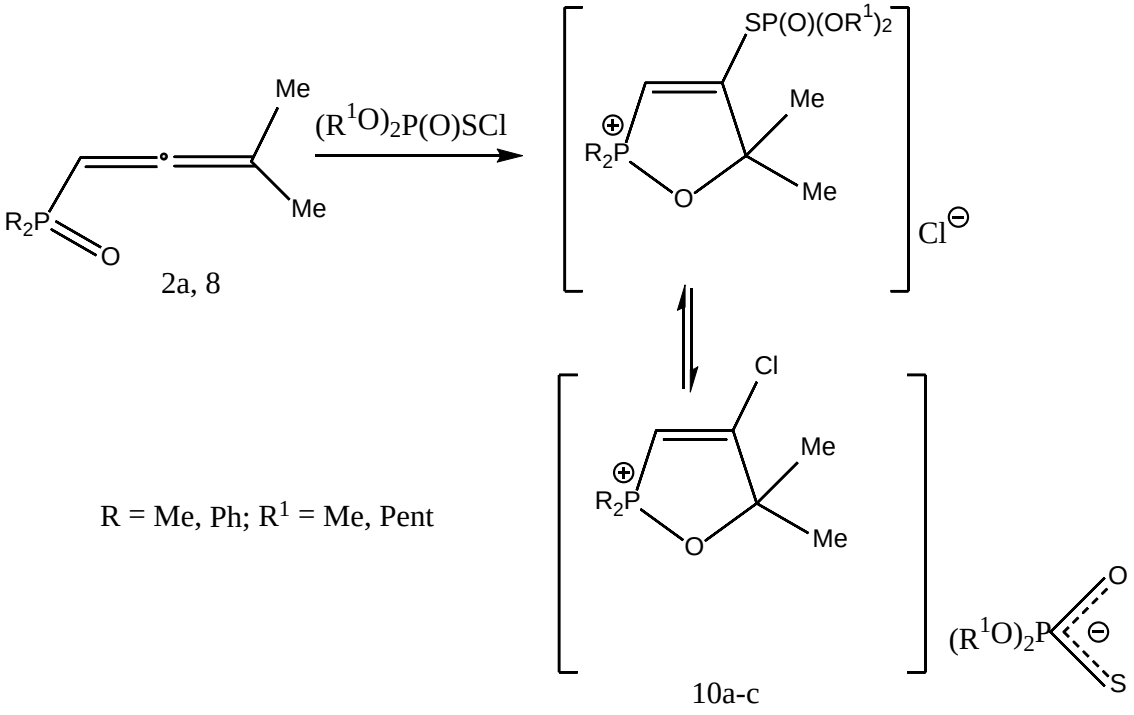

10a, $C_{17}H_{35}O_4P_2SCl$; powder (80%); Calcd.: P 14.31, S, 7.40, Cl, 8.19 %, Found: P 14.29, S, 7.37, Cl, 8.11 %; IR(KBr) νmax/cm-1 1598 (C=C), 1235 (P=O), 980 (P-O-C), ^{1}H NMR (100MHz, $CDCl_3$), δ/ppm : 6.19 [dd, $^2J_{HP}$ 23.12 Hz, 12.45 1H, (HC=)]; 1.70 [s, 3H, (CH_3)]; 0.94 [s, 3H, (CCH_3)]; 0.96 [s, 3H(CCH_3)]; 0.98[s, 3H, ($CH_3CH_2CH_2CH_2CH_2$)]; 3.68[m,8H, ($CH_3CH_2CH_2CH_2CH_2$)]; ^{31}P NMR (H_3PO_4): 110.00, 16.55

10b, $C_{27}H_{39}O_4P_2SCl$; powder (85%); Calcd.: P 11.12, S, 5.75, Cl, 6.39 %, Found: P 10.98, S, 5.71, Cl, 6.31 %; IR(KBr) νmax/cm-1 1587 (C=C), 1240 (P=O), 1000 (P-O-C), ^{1}H NMR (100MHz, CDCl3), δ/ppm : 5.95 [dd, $^2J_{HP}$ 24.73 Hz, 13.84 1H, (HC=)]; 7.75 [m, 5H,(Ph)]; 1.41 [s, 3H, (CH_3)]; 0.98[s, 3H, ($CH_3CH_2CH_2CH_2CH_2$)]; 3.84[m,8H, ($CH_3CH_2CH_2CH_2CH_2$)]; ^{31}P NMR (H_3PO_4): 109.87, 16.39

10c, $C_{19}H_{23}O_4P_2SCl$; powder (85%); Calcd.: P 13.92, S, 7.20, Cl, 7.96 %, Found: P 13.90, S, 7.19, Cl, 7.92 %; IR(KBr) νmax/cm-1 1595 (C=C), 1250 (P=O), 950 (P-O-C), ^{1}H NMR (100MHz, $CDCl_3$), δ/ppm : 6.12 [dd, $^2J_{HP}$ 24.89 Hz, 16.85 1H, (HC=)]; 7.80 [m, 5H,(Ph)]; 1.52 [s, 3H, (CH_3)]; 0.81[s, 3H, (CH_3)]; 0.95 [s, 3H, (CH_3)]; ^{31}P NMR (H_3PO_4): 107.90, 16.34

Conclusions

All the results described show that all the factors promoting the formation of quasiphosphonium intermediate in the reactions of 1,2-alkadienephosphonates with electrophilic reagents are critical for the isolation of oxaphosphole derivatives as final products.

Corresponding author: d.enchev@shu.bg

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Corresponding author: d.enchev@shu.bg
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