

The Behavior of 1,7,7 – Trimethyl Bicyclo [2.2.1] Heptane -2,3- Dione And 3-(2-Phenylhydrazono) -1,7,7- Trimethyl Bicyclo [2.2.1] Heptane -2- one Toward Organophosphorus Reagents.

Hoda Anwar Abdel-Malek

Department of Organometallic and Organometalloid Chemistry, National Research Centre, Giza, 12622, Egypt
hodanwar@yahoo.com

Abstract: heptanedione **1** reacts with tris(dialkylamino) phosphines (**3a,b**) to give dipolar product **6a,b**. Phosphate product of type **9** are produced upon reacting phenylhydrazone **2** with trialkylphosphites **4a-c**. Also, reaction of phenylhydrazone **2** with Lawesson's reagent (LR, **5**) gave adducts **10** and **11**. Structural elucidation for the new products was based upon compatible analytical and spectral data.

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Kew Words: Heptanedione, phenylhydrazone heptanone, tris(dialkylamino) phosphines, trialkyl phosphites and Lawesson's Reagent.

1. Introduction

Heptanone derivatives **1** and **2** (camphorquinones) are reported to possess a variety of pharmacological importance such as dentin - bonding agents [1], dental cements [2], and in root canal filling materials [3]. This together with our interest in organophosphorus chemistry [4-12] enhanced the synthesis of new phosphorus compounds. The present investigation has aimed to study the reaction of 1,7,7 -trimethyl- bicyclo [2.2.1] heptane -2,3- dione (**1**) with tris (dialkylamino) phosphines (**3a,b**) and 3- (phenyl hydrazone) -1,7,7-trimethyl bicyclo [2. 2.1] heptane-2-one (**2**) with trialkyl phosphite (**4a-c**) and 1,3,2,4-dithiadiphosphetane - 2 , 4 - disulfide (LR) (**5**) (Scheme 1).

2. Experimental

Melting points were determined in open glass capillaries using an Electrothermal IA 9000 series digital melting point apparatus (Electrothermal, Essex, UK) and were uncorrected. The IR spectra were measured in KBr pellets with a Perkin-Elmer Infracord Spectrophotometer model 157(Grating). The ¹H and ¹³C-NMR spectra were recorded in CDCl₃ as solvent on a Joel-500 MHz spectrometer, and the chemical shifts were recorded in δ values relative to TMS. The ³¹P-NMR (125 MHz) spectra were taken with a Varian CFT-20 (vs. external 85% H₃PO₄ standard). The mass spectra were performed at 70 eV on a Shimadzu GCS-OP 1000 Ex spectrometer provided with a data system. Elemental analyses were performed using an Elmenter Varu EL Germany Instrument.

Reaction of tris(dimethylamino)phosphine (**3a**) with 1,7,7- trimethyl-bicyclo [2.2.1] heptane -2,3-

dione (**1**)

An excess of amino phosphine **3a** (≈ 3ml) was added to **1** (0.16 g, mmol) and was heated for 5h. The reaction mixture was evaporated under reduced pressure and the residue was chromatographed on a silica gel column to give product **6a** 4,7,7 trimethyl -3- (tris (dimethylamino) phosphoniooxy) bicyclo [2.2.1] hept-2-en-olate, using methanol / chloroform as an eluent (5 / 95 , v/v), product **6a** was separated as colorless crystals, yield 73% and m.p. 221-222°C (methanol / chloroform). IR [ν, cm⁻¹, KBr]. 1590 (C=C), 1490 (enolate, carbonyl), 1310 and 870 [P-N (CH₃)₂], ¹H-NMR (500 MHz, δ ppm, CDCl₃) : 0.99 (s, 3H, CH₃), 1.03 (s, 6H, 2CH₃), 1.25 - 1.43 (m, 2H, 2CH₂), 1.62 - 1.86 (m, 2H, CH₂), 2.33 (m, H, CH), 2.65 (d, 18H, 6CH₃, J_{HP}=10.50Hz). ¹³C-NMR (125 MHz, δ ppm, CDCl₃) : 18.32 (CH₃), 19.91 (2CH₃), 26.95, 29.96 (2CH₂), 39.75 (CH), 46.03 (C(CH₃)₂), 49.25 (C-CH₃), 37.83 (N (CH₃), 101.01 (C=C-O), 189.03 (C=C-O-P). ³¹P-NMR (δ, ppm, CDCl₃) : +38.73. MS m/z (%) 329 [M⁺](50). Anal. Calcd for C₁₆H₃₂N₃O₂P (329.22) : C, 58.34 ; H, 9.79 ; N, 12.76 ; P, 9.40 . Found : C, 58.53 ; H, 9.43 ; N, 12.42 ; P, 9.82.

Similarly, 1,7,7 - trimethyl - bicyclo [2.2.1] heptane - 2,3 - dione (**1**) react with tris(diethylamino)phosphine (**3b**) to give **6b** 4,7,7 - trimethyl -3- tris (diethylamino)phosphoniooxy bicyclo [2.2.1] hept-2-en-olate (**6b**, C₂₂H₄₄N₃O₂P).

Eleuent : methanol / chloroform (5/95 , v/v). product **6b** was separated as colorless crystals yield 67 % and m.p 234-235 °C (methanol / chloroform) . IR [ν, cm⁻¹, KBr]: 1585 (C=C), 1489 (enolate , carbonyl) 1312 and 875 (P-N (CH₂CH₃)₂). ¹H-NMR (500) MHz, δ ppm, CDCl₃) : 0.99 (s, 3H , CH₃), 1.03 (s, 6H, 2CH₃), 1.25 -1.43 (m, 2H, 2CH₂), 1.62 –

1.86 (m, 2H, CH₂), 2.35 (m, H, CH), 0.95, 1.35 (2t, 18H, P[N(CH₂CH₃)₂]₃), 2.85, 3.25 (m, 12H, P[N(CH₂CH₃)₂]₃). MS m/z (%) 413 [M⁺] (90), corresponding to the molecular formula C₂₂H₄₄N₃O₂P. Anal. Calcd. for C₂₂H₄₄N₃O₂P (413.58) : C, 63.89 ; H, 10.72 ; N, 10.16 ; P, 7.49. Found : C, 63.52, H, 11.11 ; N, 10.49 , P, 7.23.

Reaction of trimethyl phosphite 4a with 3-(2-phenylhydrazono) - 1,7,7 - trimethyl bicyclo[2.2.1] heptane -2-one (2)

Trimethyl phosphite (**4a**) (0.12g , 1m mol) was added drop wise to a solution of compound **2** (0.25g , 1 m mole) in dry toluene (30 mL) , and the reaction mixtur was refluxed for 5h. after evaporation the volatile material under reduced pressure, the residue was applied to a silica gel column chromatography to give product **9a** dimethyl 1,7,7 - trimethyl -3-(2-phenylhydrazinyl)bicyclo [2.2.1] hept -2-en-ylphosphate (**9a**, C₁₈H₂₇N₂O₄P).

Eluent: Petroleum ether / ethyl acetate (95/5,v/v), **9a** was separated as colorless crystals yield 65%. and m.p 153-154 °C. IR [ν, cm⁻¹, KBr] : 3328 (NH) 3275 (NH), 1603 (C=C) and 1260 (P=O). ¹H-NMR (500 MHz, δ ppm, CDCl₃) : 0.98 (s, 3H , CH₃), 1.11 (s, 6H₃, 2CH₃), 1.22-1.40 (m, 2H, CH₂), 1.51-1.63 (m, 2H, CH₂), 2.53 (m, H, CH), 3.83 (d, 6H ³J_{HP} = 11.50 Hz, (O)P (OCH₃)₂), 7.13 – 7.38 (m, 5H, aromatic) and 11.13 (s, 1H , NH), 11.85 (s, 1H, NH) . ¹³C-NMR (125 MHz, δ ppm, CDCl₃) : 17.43 (CH₃), 20.52 (2CH₃), 22.16, 30.15(2CH), 39.90 (CH), 46.75 (C-(CH₃)₂), 49.80 (C-CH₃), 53.70 (d, ²J_{CP}=29.30, O=P(OCH₃)₂), 121.51 (C=C-NH), 160.52 (C=C-O). ³¹P-NMR (δ ppm, CDCl₃) : +1.85. MS m/z (%) 366 [M⁺] (75). Anal. Calcd. for C₁₈H₂₇N₂O₄P(366.17) : C, 59.01 ; H, 7.43 ; N, 7.65 ; P, 8.45. Found: C, 59.42; H, 7.71 ; N, 7.29 ; P, 8.83.

Reaction of triethyl phosphite (4b) with 3-(2-phenyl hydrazono) 1,7,7 – trimethyl bicyclo [2.2.1] heptane -2-one(2)

The same method described for **9a** to give adduct **9b** diethyl 1,7,7 - trimethyl -3-(2-phenyl hydrazinyl) bicyclo [2.2.1] hept -2-en-2-yl phosphate (**9b**, C₂₀H₃₁N₂O₄P). Eluent: petroleum ether / ethyl acetate (95/5, v/v). product **9b** was separated as colorless crystals yield 70% and m p 168-169°C.

IR [ν, cm⁻¹, KBr] : 3327 (NH), 3270 (NH), 1601 (C=C) and 1250 (P=O). ¹H-NMR (500 MHz, δ ppm, CDCl₃) : 0.99 (s, 3H, CH₃), 1.11 (s, 6H, 2CH₃), 1.25-1.42 (m, 2H CH₂), 1.52-1.64 (m, 2H, CH₂), 2.55 (m, H, CH), 1.38 (t, 6H, (O)P(OCH₂-CH₃)₂), 3.91 (m, 4H, (O)P(OCH₂ - CH₃)₂), 7.25 - 7.41 (m, 5H, aromatic) and 11.11 (s, 1H, NH), 11.79 (s, 1H, NH). MS m/z (%) 394 [M⁺] (55). Anal. Calcd. for

C₂₀H₃₁N₂O₄P(394.20) : C, 60.90 ; H, 7.92 ; N, 7.10 ; P, 7.58. Found : C,60.53 ; H, 8.21 ; N, 7.33 ; P, 7.93.

Similarly, 3-(2-phenyl hydrazono) -1,7,7-trimethyl bicyclo [2.2.1] heptane - 2 - one (**2**) reacted with triisopropylphosphite (**4c**) to give **9c** diisopropyl 1,7,7 - trimethyl -3- (2- phenyl hydrazinyl) bicyclo [2.2.1] hept-2-en-ylphosphate (**9c**, C₂₂H₃₅N₂O₄P). Eluent : petroleum ether / ethyl acetate (95/5, v/v). Product **9c** was separated as colorless crystals yield 63% and m.p 175 - 176°C . IR [ν, cm⁻¹, KBr] ; 3325 (NH), 3269 (NH), 1600 (C=C) and 1255 (P=O). ¹H-NMR (500 MHz, δ ppm, CDCl₃) : 0.99 (s, 3H, CH₃), 1.12 (s, 6H, 2CH₃), 1.22 – 1.40 (m, 2H CH₂), 1.55 – 1.65 (m, 2H, CH₂), 2.55 (m, H, CH), 1.23 [m, 12H (O)P(O-CH (CH₃)₂)₂], 4.34 - 4.73 [2m, 2H, (O)P(O-CH (CH₃)₂)₂], 7.25 – 7.42 (m, 5H, aromatics) and 11.10 (s, 1H, NH), 11.75 (s, 1H, NH). MS m/z (%) 422 [M⁺] (40). Anal. Calcd for C₂₂H₃₅N₂O₄P(422.50) : C, 62.54 ; H, 8.35 ; N, 6.63 ; P, 7.33. Found : C, 62.32 ; H, 8.41 ; N, 6.52 ; P, 7.55.

Reaction of Lawesson's reagent (5) with 3-(2-phenyl hydrazono) 1-,7,7 – trimethyl bicyclo [2.2.1] heptane -2-one(2)

A mixture of **5** (0.4g , 1 m mol). and **2**(0.25g , 1 m mol) in dry toluene (40 mL). The reaction mixture was refluxed for 15 h. The reaction mixture was evaporated under reduced pressure and the residue was applied to a silica gel column chromatography, using petroleum ether/ethyl acetate as eluent to give products **10** and **11**, respectively. The product **10** 1,7,7-trimethyl - 3 - (2- phenylhydrazono) bicyclo [2.2.1] heptane -2- thione (**10**, C₁₆H₂₀N₂S). Eluent : petroleum ether/ethylat (98/2, v/v). It was separated as yellow crystals yield 35% and m.p 75 - 76 °C . IR [ν, cm⁻¹, KBr] ; 3227 (NH), 1175 (C=S) ¹HNMR (500 MHz, δ ppm, CDCl₃) : 0.99 (s, 3H, CH₃), 1.15 (s, 6H, 2CH₃), 1.25 - 1.43 (m, 2H CH₂), 1.55 – 1.65 (m, 2H, CH₂), 2.56 (m, H, CH), 7.28 - 7.47 (m, 5H, aromatics) and 11.66 (s, H, NH). ¹³C-NMR (125 MHz, δ ppm, CDCl₃). 18.55 (CH₃), 20.22 (2CH₃), 27.11, 31.33 (2CH₂), 47.50 (C-(CH₃)₂), 49.88 - (C-CH₃), 34.99(CH) and 240.33 (C=S). MS m/z (%) 272 [M⁺] (100). Anal. Cald for C₁₆H₂₀N₂S (272.41) : C, 70.55 ; H, 7.40 ; N, 10.28 ; S, 11.77 found : C, 70.75 ; H, 7.82 ; N, 10.59 ; S, 11.65.

2'-(4-methoxyphenyl) - 4 , 7 , 7 -Trimethyl -3-(phenylamino) 3H - spiro [bicyclo [2.2.1] heptane - 2, 4' - [1,3,2] thiazaphosphetidine] - 3'- thione (**11** , C₂₃H₂₇N₂O₃PS₃).

Eluent : petroleum ether / ethylacetate (95/5 , v/v). Product **11** was separated as colorless crystals, yield 55% and m.p. 138 – 139°C. IR (ν, cm⁻¹, KBr): 3210 (NH), 1175 (C=S) . ¹H-NMR (500 MHz , δ ppm, CDCl₃) : 0.99 (s, 3H, ct₁₃), 1.15 (s,6H ,

2CH₃), 1.25 - 1.43 (m, 2H, CH₂), 1.55 - 1.65 (m, 2H, CH₂), 2.66 (m, H, CH), 3.85 (s, 3H, OCH₃), 7.15 - 7.95 (m, 9H, aromatics), 11.55 (NH). ¹³C-NMR (125 MHz, δ ppm, CDCl₃): 18.56 (CH₃), 20.24 (2CH₃), 27.31, 31.35 (2CH₂), 47.55 (C - (CH₃)₂), 49.88 (C - CH₃), 55.80 (C - OCH₃), 160.61 (C = C-O) and 243.21 (C = S). ³¹P-NMR (δ ppm, CDCl₃): + 89.99. MS m/z (%) 474 (55). Anal. Calcd. for C₂₃H₂₇N₂OPS₃ (474.10): C, 58.20, H, 5.73, N, 5.90; P, 6.53, S, 20.27. Found: C, 58.53, H, 5.93; N, 5.49, P, 6.71, S, 20.35.

3. Results and Discussion

When heptanedione **1** is allowed to react with tris (dimethylamino) phosphine (**3a**) [8] without solvent was heated 5h to gave the open dipolar adduct 4,7,7 trimethyl -3- (tris (dimethylamino) phosphoniooxy) bicyclo [2.2.1] hept -2-en-2-olate (**6a**). Compound **6a** are chromatographically pure and posses sharp melting point. The structure of compound **6a** was identified for the following reasons: Elemental and mass spectral analyses for compound **6a** corresponded to empirical formula of C₁₆H₃₂N₃O₂P. The IR of **6a** (KBr, cm⁻¹) exhibited strong absorption bands at 1310, 870 cm⁻¹ P[N(CH₃)₂]₃ [13] and absence of band at 1700 (C=O camphor). The ¹H-NMR spectrum (in CDCl₃) of the adduct showed doublet centered at δ = 2.65 ppm (J_{HP} = 10.50 Hz) due to 18 H of the dimethylamino group attached to the phosphorus atom of the [N(CH₃)₂]₃ moiety [14]. The ³¹P-NMR spectrum of **6a** exhibited signal at δ = +38.73 ppm (85% H₃PO₄). The formation of the open dipolar ion **6a** might arise [15] by the nucleophilic attack of the phosphorus of **3a** on the carbonyl carbon in heptanequinone **1**. Our results rule out the possibility of the formation of compounds having the cyclic structure **7** since the latter would predict a negative value for the signal of ³¹P-NMR corresponding to the structure **7** (Scheme 2).

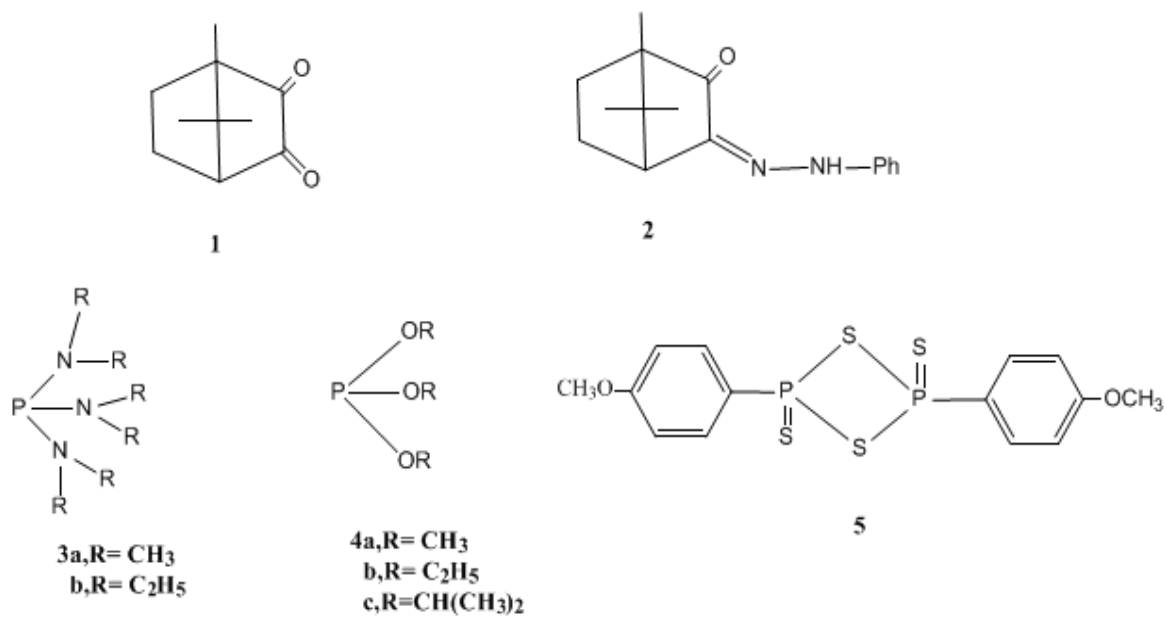
Similarly, the reaction of **1** with tris (diethylamino) phosphine (**3b**) proceeded without solvent to give chromatographically pure adduct **6b**. Structure elucidation for compound **6b** was attested by analytical and spectral data (cf. Experimental).

Next, the study was extended to include the behavior of 3-(2-phenylhydrazono) -1,7,7- trimethyl bicyclo [2.2.1] heptane-2- one (**2**) toward trimethyl phosphite (**3a**) [16] in dry toluene proceeded at the reflux temperature to give a chromatographically pure 1:1 adduct formulated as dimethyl-1,7,7-trimethyl-3-(2-phenylhydrazinyl) bicyclo [2.2.1] hept -2-en-2-ylphosphate (**9a**) (Scheme 3), was deduced from its elemental analysis, IR ¹H, ¹³C, ³¹P-NMR, and mass spectral data (cf.

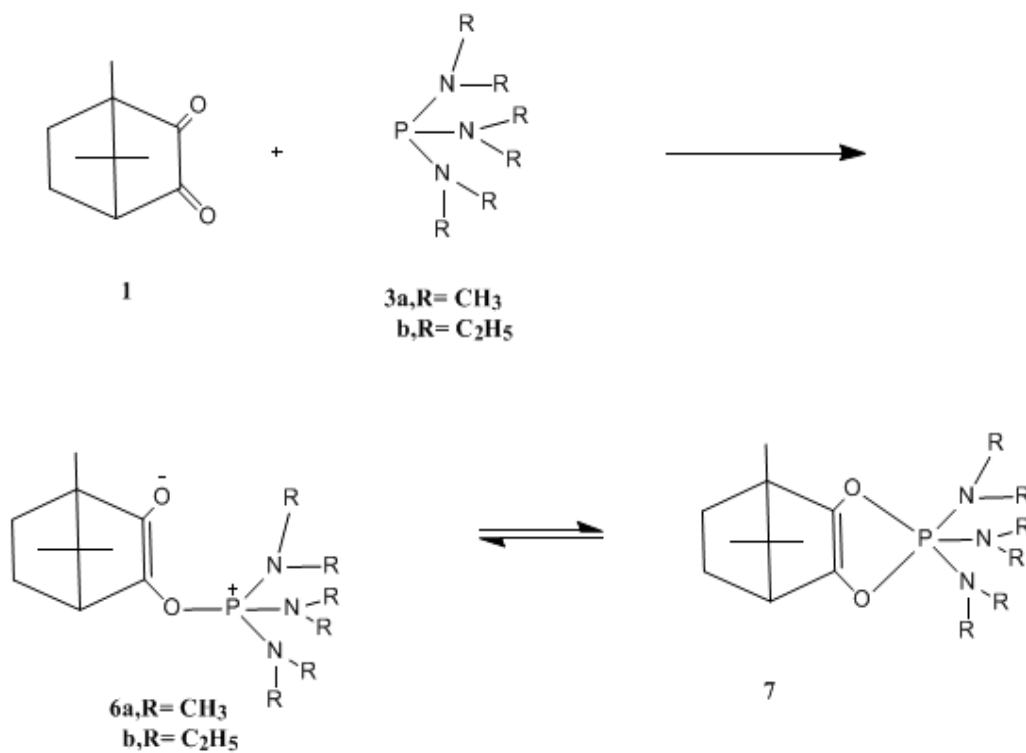
Experimental). Similarly **4b** and **4c** reacted with **2** to give dialkyl phosphate **9b** and **9c** respectively, in good yields (scheme 3). Structure assignments for **9b** and **9c** were substantiated on the basis of their elemental analysis and spectral data. (cf. Experimental)

A possible explanation for the course of the reaction of trialkylphosphites **3a-c** with **2** was shown in Scheme 3. The reaction was assigned to proceed through an initial attack of the phosphorous reagents **3a-c** at the most reactive center in **2** and led to the formation of the dipolar adduct **8**. The reaction was accompanied with rapid hydrolysis by the presence of unavoidable moisture and elimination of one molecule of alcohol under the applied reaction conditions to afford the dialkyl phosphate products (**9a-c**) (Scheme 3).

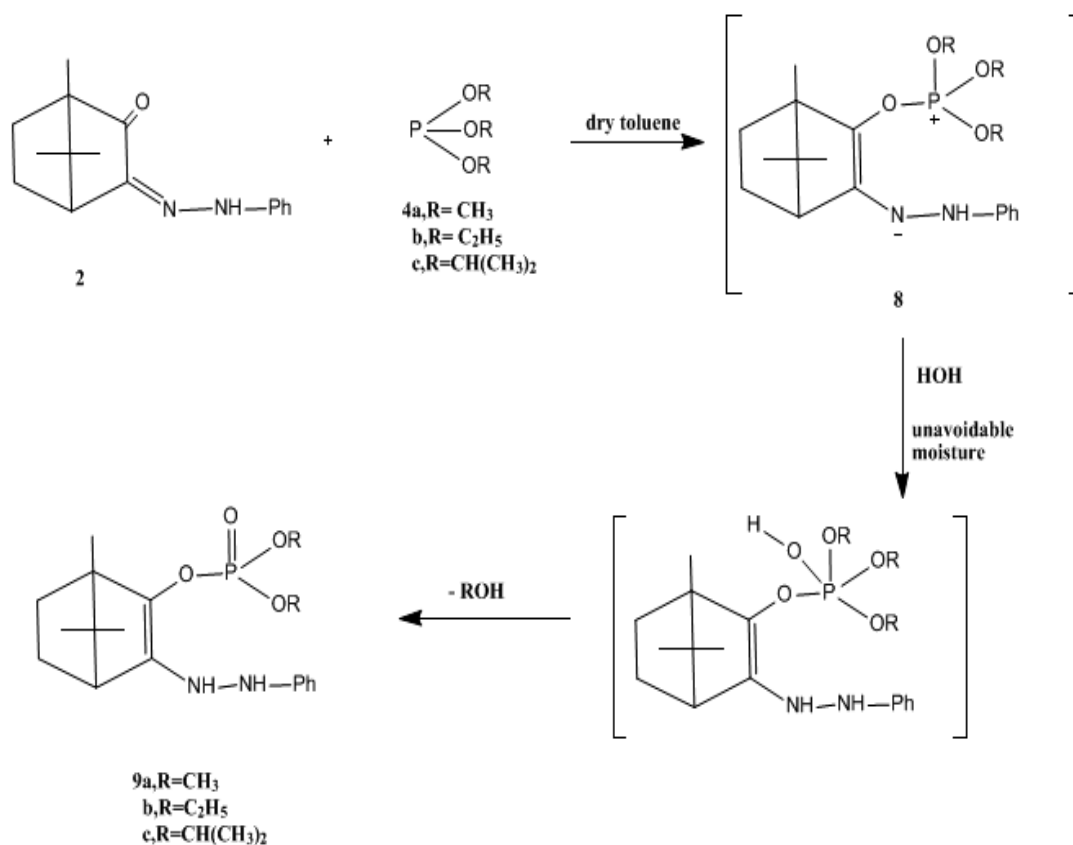
Furthermore, this study was extended to include the reaction of Lawessen's reagent **5**[7,11] with **2**. It was found that, when one mole of **2** was allowed to react with one equivalent of **5** in refluxing toluene for 15 h. A mixture of **10** and **11** were obtained. Compounds **10** and **11** are chromatographically pure and possess sharp melting points. Compound **10** (yield 35%) was formulated as 1,7,7 trimethyl -3-(2-phenylhydrazono) bicyclo [2.2.1] heptane -2-thione based upon analytical and spectroscopic arguments (cf. Experimental). The second product **11** (yield 55%) was formulated as the thiated cyclic 2'-(4-methoxyphenyl) - 4,7,7 - trimethyl -3'-(phenylamino)- 3H - spiro [bicyclo [2.2.1] heptane - 2,4 - [1,3,2] thiazaphosphetidine] -3³- thione, for the following reasons: Elemental and mass spectral analyses for compound **11** corresponded to an empirical formula of C₂₃H₂₇N₂OPS₃. The structure assigned for compound to **11** was based on the ³¹P-NMR shift at δ = +89.99 ppm (85% H₃PO₄), which corresponded to a cyclic structure [7, 17]. The IR spectrum of **11** (KBr, cm⁻¹) showed absence of bands at 1700 cm⁻¹ (C=O) and at 1648 cm⁻¹ (C=N) of phenylhydrazone heptanone of compound **2**. The ¹H-NMR spectrum of **11** (CDCl₃, δ ppm) revealed the presence of signals at 7.15 - 7.95 ppm (m, 9H) corresponding to the aromatic protons and at 3.85 ppm (s, 3H, OCH₃). The ¹³C-NMR (CDCl₃, δ ppm) revealed absence of a signal of carbonyl group of the starting material **2** at 204.83 (C=O) and appear signal at 243.21 (C = S). The mass spectrum of **11** contained a prominent peak of M⁺ at m/z 474 (85%) which supported the thiated, cyclic structure **11**. compound **11** was formed via the thiation by usual manner and the addition of LR **5** to the carbonyl group (C=O) and (C=N) group of hydrazone of the starting material **2** (Scheme 4).



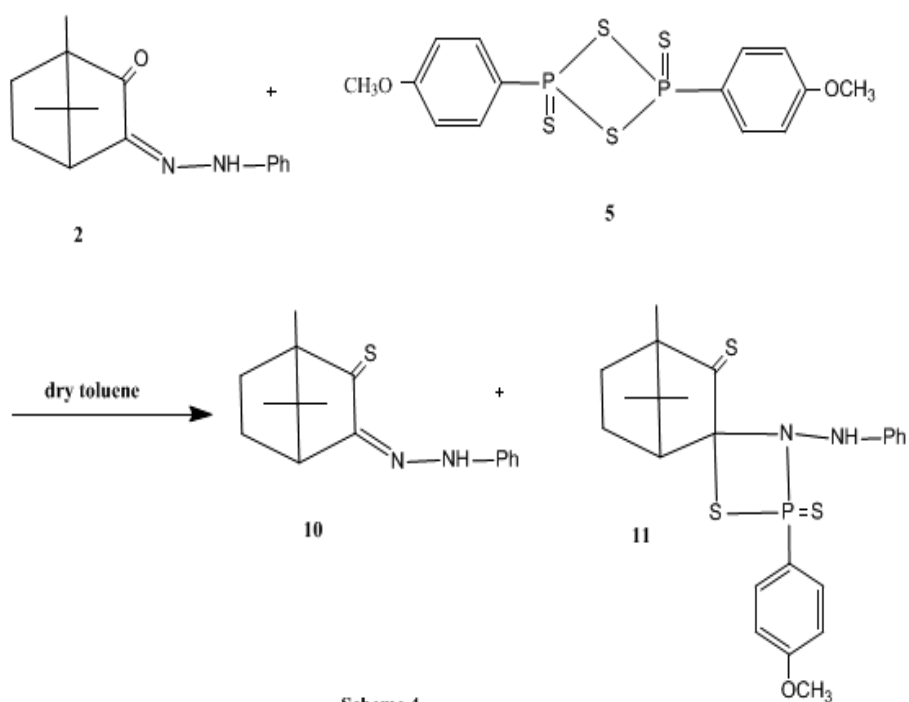
Scheme 1



Scheme 2



Scheme 3



Scheme 4

Conclusion

From the present study, it was shown that 1,7,7 - trimethyl bicyclo [2.2.1] heptane- 2,3- dione (**1**) reacted with tris (dialkylamino) phosphines **3a,b** gave the dipolar adducts **6a,b**. On the other hand 3-(2-phenylhydrazonon) – 1,7,7-trimethyl bicyclo [2.2.1] – heptane -2-one(**2**) reacted with trialkylphosphite **4a-c** gave phosphate **9a-c**. Also, **2** reacted with LR **5** to give thiated product **10** and led to new thiated cyclic adduct **11**. The different adducts whose structures vary according to the nature of the phosphorus reagents as well as on the stability of the addition products.

Corresponding author

Hoda Anwar Abdel – Malek
Department of Organometallic and Organometallic chemistry
National Research centre, Giza, 12622, Egypt
E-mail: hodanwar@yahoo.com

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