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Chemistry of Phosphorus Ylides, Part 30. Reaction of Camphorquinone Derivatives with Active Phosphacumulenes and Stabilized Phosphonium Ylides

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THE REACTION of the bifunctional camphorquinone(1) , its monophenylhydrazone (13) and monooxime (16) with the active phosphacumulenes (2) was performed. Phosphanylidene- cyclobutylidenes (5), azitidine bicyclo heptanones (14) and phosphanylidenes (17) were obtained, respectively. On the other hand, the stabilized phosphonium ylides (6) react with the above mentioned substrates (1, 13, and 16) to give the corresponding oxaphosphetane (8), phosphanylidene (10) oxatricycloundecadiene (12), azaphosphetidines (15) and the azatricyclo- undecadienone (19).

Keywords: Camphorquinone derivatives, phosphonium ylides, Phosphanylidene cyclobutylidenes, Oxaphosphetane and Azatricycloundecadienone.

Camphorquinone and its derivatives constitute an important class of organic compounds with pharmacological importance. The most interesting aspects of these compounds are their applications in permanent restorative dental resins [1-3] , as substrate in dental cements [4,5] , dentin-bonding agents [6,7] , and in root canal filling materials [1] . In continuation to our work in the field of phosphonium ylides [8-14] , the present investigation has aimed to investigate the reaction of camphorquinone and its derivatives, such as, 1,7,7-trimethyl- bicycle [2.2.1]-heptane-2,3-dione (1), 3-(2-phenylhydrazono)-1,7,7-trimethylbicyclo [2.2.1]-heptan-2-one (13), and 3-(hydroxyimino)-1,7,7-trimethylbicyclo[2.2.1] heptan-2-one (16) with the active nucleophilic phosphacumulene reagents, namely (N-phenyliminovinylidene) -(2a), (2-oxovinylidene) - (2b), and (2-thioxovinylidene) - triphenylphosphorane (2c). These active phosphacumulene ylides are important phosphorus reagents, used for the synthesis of heterocyclic phosphorus compounds [15,16] . A comparative study on the behavior of camphorquinone 1 and its derivatives 13, and 16 toward stabilized phosphonium ylides namely, methoxycarbonyl- (6a), and ethoxycarbonyl-methylenetriphenylphosphorane (6b) has been performed, too.

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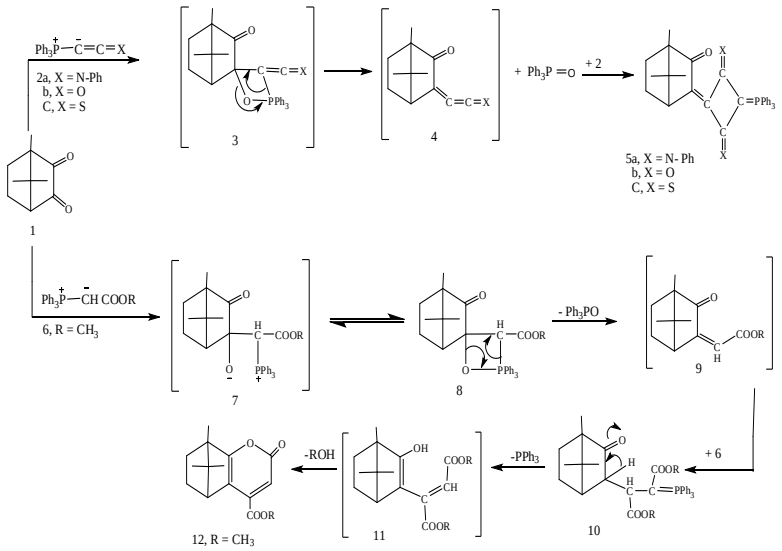
Results and Discusion

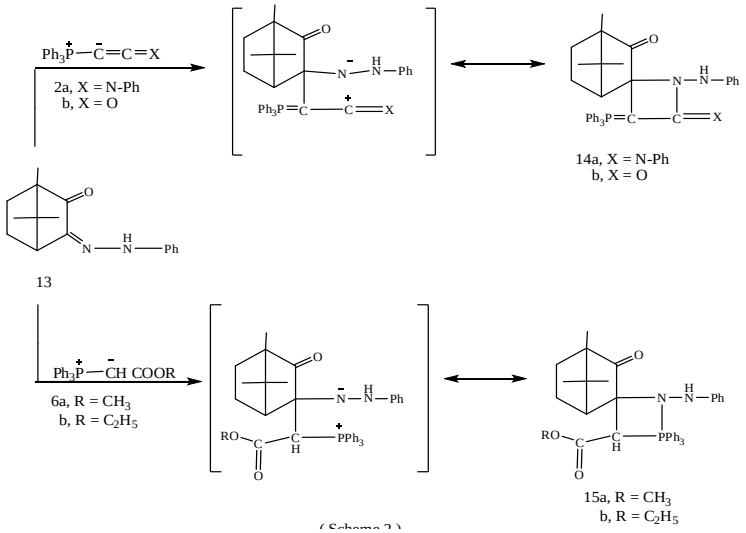
We have found that the reaction of camphorquinone (1) with (2) mole-equivalents of (N-phenyliminovinylidene) triphenylphosphorane (2a), in tetrahydrofuran at room temperature for 10hr, triphenylphosphine oxide together with the phosphanylidene cyclobutylidene camphorquinone (5a) were obtained. Structural support for compound 5a was based upon spectroscopic data and molecular weight determination (MS). The IR spectrum of 5a (KBr, cm^{-1}) showed strong absorption bands at 1700 (C=O), 1577 (C=N), and 1463 (P-Phenyl) [17] . The ^{1}H NMR spectrum of 5a ($CDCl_3$, δ ppm) showed signals at 0.99 (s, 3H, CH_3), 1.03 (s, 6H, $2CH_3$), 1.25-1.43 (m, 2H, CH_2), 1.62– 1.86 (m, 2H, CH_2), 2.33 (m, H, CH), and 7.32-7.93 (m, 25H, aromatics). Its ^{13}C NMR spectrum ($CDCl_3$, δ ppm) showed signals at 18.32 (CH_3), 19.91 ($2CH_3$), 26.95, 29.96 ($2CH_2$), 39.75, (CH), 46.03 ($\underline{C}$- $(CH_3)_2$), 49.25 ($\underline{C}$-CH_3), 133.25 (C=P), 169.55 (C=N), and 205.33 (C=O). A signal at δ =15.5 ppm was observed in its ^{31}P NMR which fits with the phosphorane on a four –membered ring [18,19]. In the MS of 5a an ion peak at m /z = [262(PPh_3) 100 %] was observed. Moreover, the reaction of compound 1 with 2 moles of phosphacumulenes (2b and 2c) proceeded in dry toluene under reflux for 12hr in case of 2b, 14hr with 2c, to give triphenylphosphine oxide together with 5b or 5c. Compounds 5a-5c were equally obtained, irrespective whether 2 or 4 mole equivalents of the phosphacumulenes (2a-2c) were used. Formation of compounds 5a-5c occurs by the [2+2] –cycloaddition of one carbonyl group in the camphorquinone (1) to the ylidic C-P of the phosphacumulenes (2) to give the oxaphosphetanes (3) as intermediates [20-22] . Triphenylphosphine oxide was eliminated with the formation of the unstable ketenes (4), [23] which add a second molecule of the active ylides (2) by a [2+2] cycloaddition to give phosphanylidene-cyclobutylidene camphorquiones (5a-5c) (Scheme1).

When camphorquinonephenylhydrazone (13) was treated with (N-phenyl-iminovinylidene) -(2a) or (2-oxovinylidene)-triphenylphosphorane (2b) in dry THF and refluxed for 10hr in the case of 2a, 14hr when 2b was used, the yellow adducts (14a and b) were isolated in good yields. Compounds 14a and 14b were obtained in the same yields irrespective whether 1 or 2 mole equivalents of the phosphacumulenes (2) were used. Molecular weight determinations (MS) and spectroscopic results were consistent with the assigned structures of compounds 14a and 14b. The IR spectrum of the phosphorane (14a) (KBr, cm^{-1}) revealed the absence of absorption band for (C=N) group of hydrazone (13) and showed the presence of strong absorption bands at ν =3257(NH), 1702 (C=O), 1625 (C=N, ylide), and 1448 cm^{-1} (P-Phenyl). The ^{1}H NMR spectrum of 14a (DMSO, δ ppm) showed signals at 0.98 (s, 3H, CH_3), 1.11 (s, 6H, $2CH_3$), 1.22- 1.40 (m, 2H, CH_2), 1.50-1.65 (m, 2H, CH_2), 2.53 (m, H, CH), 7.13-7.38 (m, 25H, aromatic), and the (NH) proton resonated at δ =11.53 (exchangeable with D_2O) ppm. In its ^{13}C NMR spectrum (DMSO, δ ppm), signals were recoded at 17.48 (CH_3), 20.62 ($2CH_3$), 22.16, 30.13 ($2CH_2$), 39.97 (CH), 46.73($\underline{C}$-$(CH_3)_2$), 49.88($\underline{C}$-CH_3), 143.54 (C=P), 156.65 (C=N), and 202.83(C=O). The ^{31}P NMR

shift was recorded for 14a at δ=19.37 ppm. Its mass spectrum indicated the presence of ion peak at m/z= [256 camphorquinonephenylhydrazone, 13.86%], which originate *via* the cleavage of the molecular ion peak at m /z = 633[M^+]. Compounds 14a and 14b were formed *via* the addition of phosphacumulenes (2a or 2b) to the phenylhydrazone C=N group rather than the (NH) or carbonyl group of phenylhydrazone of the starting material 13 (Scheme 2).

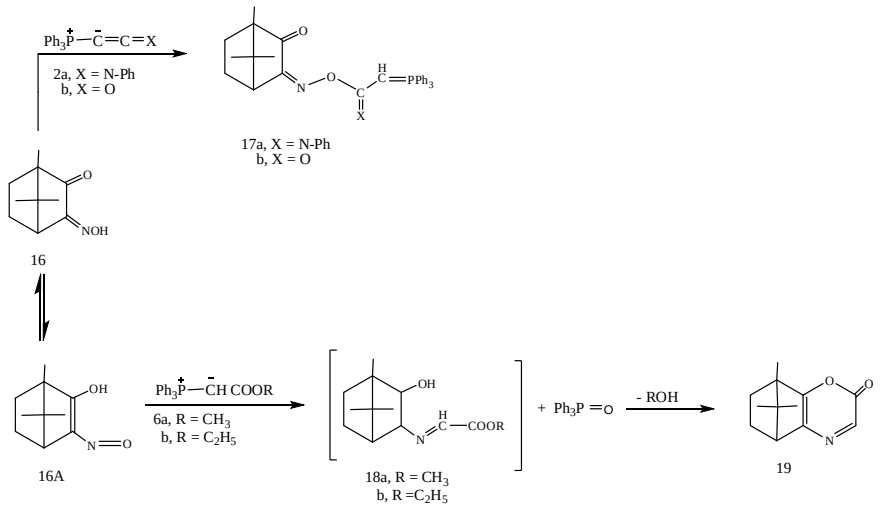


Scheme 1



Scheme 2

When camphorquinone oxime (16) was reacted with phosphacumulene ylides (2a or 2b) in 1:1 molar ratio in dry boiling toluene for 8hr in case of 2a and 12hr in case of 2b, to give the corresponding phosphoranes (17a and 17b). Structural assignments for 17a and b were supported by spectroscopic data. The IR spectum of 17a (KBr, cm^{-1}) confirmed the proposed structure showing no absorption band for the =N-OH group, and revealed the presence of strong absorption bands at ν1706 (C=O), 1682, 1648 (2C=N), and 1485 (P-Phenyl). Its ^{1}H NMR spectrum ($CDCl_3$, δ ppm) displayed signals at 0.99 (s, 3H, CH_3), 1.01 (s, 6H, $2CH_3$), 1.38-1.63 (m, 2H, CH_2), 1.69-1.89 (m, 2H, CH_2), 2.53 (m, H, CH), 4.24 (d, H, CH=P, $^{2}J_{HP}$=24.15 Hz), and 7.15-7.42 (m, 20H, aromatic), whereas its ^{13}C NMR spectrum ($CDCl_3$, δ ppm) revealed the presence of signals at 18.07 (CH_3), 20.63 ($2CH_3$), 22.77, 29.77 ($2CH_2$), 39.54 (CH), 44.52 (C-$(CH_3)_2$), 48.30 (C-(CH_3), 139.37 (C=P), 154.21, 158.45 (2C=N), and 201.01(C=O). The ^{31}P NMR shift recorded for 17a was at δ= -19.54 ppm. The MS of 17a was found at m/z = [283 (M^{+}- (CH=PPh_3)10.95%, and 278 (Ph_3PO) 62.02%]. Formation of compounds 17a and 17b occurs *via* the addition of phosphacumulenes (2a or 2b) to the OH group rather than the carbonyl group of oxime (16) (Scheme 3).



Scheme 3

The behavior of the stabilized phosphonium ylides (6a and 6b) towards camphorquinone 1 and its derivatives 13, and 16 was also studied to determine the site of attack. We have found that the stabilized phosphonium ylide, namely methoxycarbonylmethylenetriphenylphosphorane (6) reacted with camphorquinone (1), in dry toluene under reflux for 8hr to give yellow three adducts 8, 10 and 12, respectively, alongwith triphenylphosphine, and triphenylphosphine oxide. Compounds 8, 10, and 12 were equally obtained whether 1 mole equivalent or 2 mole- equivalents of Wittig reagent 6 were used with respect to 1 mole equivalent of compound 1. The structures of compounds 8, 10, and 12 were

based on spectroscopic data and molecular weight determination (MS), which agreed with the proposed structures. The IR spectrum of 8 (KBr, cm^{-1}) showed strong absorption bands at 1727 (br, C=O, cyclic ketone, ester), 1451 (P-Phenyl), and 1120 due to an aromatic vibration involving some P-C stretching. The ^{1}HNMR spectrum ($CDCl_3$, δ ppm) of 8, showed singals at 0.99 (s, 3H, CH_3), 1.11 (s, 6H, $2CH_3$), 1.37-1.68 (m, 2H, CH_2), 2.06-2.18 (m, 2H, CH_2), 2.29 (m, H, CH), a doublet was observed at δ =3.00 (d, 1H, CH-P, $^{2}J_{HP}$= 23.60 Hz), 3.72 (s, 3H, OCH_3), and 7.06 - 7.12 (m, 15H, aromatic). The ^{13}C NMR spectrum of 8 ($CDCl_3$, δ ppm) showed signals at 17.72 (CH_3), 20.70 ($2CH_3$), 25.81, 29.92 ($2CH_2$), 39.95 (CH), 45.32(C-$(CH_3)_2$), 49.48 (C-CH_3), 57.23 (OCH_3), 118.12 (C-P), 166.65 (C=O, ester), and 207.03 (C=O, cyclic ketone). A signal at δ=30.71 ppm was observed in the ^{31}P NMR spectrum of 8 which fits with the phosphorane [24] . In the MS of 8 ion peaks were observed at m/z= 222 [(M^+-Ph_3PO) 61.02%, and 278 (Ph_3PO) 13.11%]. Compound 10 is quite stable, its structure was established from spectroscopic data. The IR spectrum of 10 (KBr, cm^{-1}) exhibited absorption bands at = 1733 (C=O, camphor), 1662 (br, C=O, ester), and 1448 (P-Phenyl). The ^{1}H NMR spectrum ($CDCl_3$, δ ppm) of 10 revealed the presence of signals at 0.98 (s, 3H, CH_3), 1.12 (s, 6H, $2CH_3$), 1.46-1.65 (m, 2H, CH_2), 1.86-1.99 (m, 2H, CH_2), 2.51 (m, H, CH), 2.54 (dd, CH-CH-$COOCH_3$, $^{3}J_{HH}$= 11.45 Hz, $^{4}J_{HP}$= 4.2 Hz) and 2.76 (dd, CH-C=P, methine, $^{3}J_{HH}$=11.45 Hz, $^{3}J_{HP}$= 12.55 Hz). Moreover, two singlets were found at δ= 3.70, 3.74 ppm due to the presence of two methoxy groups of the ester, and the aromatic protons appeared as multiplets in the region δ =7.01- 7.19 ppm which integrated to 15 protons. The ^{13}C NMR spectrum of 10 ($CDCl_3$, δ ppm), showed signals at 17.93 (CH_3), 20.82 (H-C-C=P), 21.24 ($2CH_3$), 26.82, 29.49 ($2CH_2$) 39.38 (CH, cyclic ketone), 45.63 (C-$(CH_3)_2$), 47.56 (CH,-CH-$COOCH_3$), 51.88 (C-CH_3), 58.22, 58.81 (2 OCH_3), 148.95 (C=P), 166.42, 168.23 (2C=O, ester), and 204.49 (C=O, camphor). In the mass spectrum of 10 ion peaks at m/z= [279(M^+- (Ph_3PO) 6.21%, 262(PPh_3) 3.84%] were found. Moreover, a signal at δ =31.03 ppm was observed in its ^{31}P NMR spectrum. The identity of compound 12 was supported by molecular weight determination (MS) as well as spectroscopic data, which are compatible with the assigned structure. The IR spectrum of 12 (KBr, cm^{-1}) disclosed the presence of strong absorption bands at 1667 (C=O, lactone), and 1662 cm^{-1} (C=O, ester). The ^{1}H NMR spectrum of 12 ($CDCl_3$, δ ppm) showed signals at 1.11 (s, 3H, CH_3), 1.26 (s, 6H, $2CH_3$), 1.35-1.58 (m, 2H, CH_2), 1.62-1.83 (m, 2H, CH_2), 2.25 (m, H, CH), 3.73 (s, 3H, OCH_3), and 5.14 (s, H, CH, aromatic). The ^{13}C NMR spectrum of 12 ($CDCl_3$, δ ppm) showed signals at 14.28 (CH_3), 21.56 ($2CH_3$), 26.67, 31.20 ($2CH_2$), 39.21 (CH, camphor), 46.82 (C-$(CH_3)_2$), 48.95 (C-CH_3), 56.12 (OCH_3), 123.55 (CH, aromatic), 163.76 (C=O, lactone), and 169.45 (C=O, ester) ppm. Its mass spectrum showed an ion peak at the m/z= [263 (M+H) 7.03%]. The reaction of Witting reagent (6a) with camphorquinone (1) is explained by the nucleophilic addition of phosphonium ylide 6a to one of the carbonyl groups of 1 to give the betaine (7), which is cyclized to the oxaphosphetane (8). Part of 8 decomposed to give the alkene (9) together with triphenylphosphine oxide. Addition of a second molecule of the stable ylide (6) to the alkene (9) to afford the phosphonium ylide

(10). Expulsion of triphenylphosphine from the intermediate betaine 10 gives the intermediate 11, which is cyclized *via* elimination of methanol to form camphorquinone derivative 12 (Scheme 1).

When camphorquinonephenylhydrazone (13) was treated with the stabilized phosphonium ylides 6, in dry boiling toluene for 10 hr in case of 6a and 12hr. when 6b was used . The adducts (15a and 15b) were obtained in good yields. The structures of compounds 15a and 15b were assigned from their spectral data. The IR spectrum of 15a (KBr, cm^{-1}) showed bands at = 3264 (NH), 1695 (br, C=O, alicyclic carbonyl, and ester), and 1509 cm^{-1} (P-Phenyl). The ^{1}H NMR spectrum of 15a ($CDCl_3$, δ ppm) showed signals at 1.02 (s, 3H, CH_3), 1.15 (s, 6H, $2CH_3$), 1.34-1.50 (m, 2H, CH_2), 1.56-1.64 (m, 2H, CH_2), 2.31 (m, H, CH), 3.12 (d, H, CH-P, $^{2}J_{HP}$=22.45 Hz), 3.62 (s, 3H, OCH_3), 7.44-7.74 (m, 20H, aromatics), and 11.87 ppm (s, H, NH, exchangeable with D_2O). Its ^{13}C NMR showed ($CDCl_3$, δ ppm) signals at 18.23 (CH_3), 21.67 ($2CH_3$), 24.17, 30.35 ($2CH_2$), 38.56 (CH, alicyclic), 43.45 ($\underline{C}$-$(CH_3)_2$), 46.3 ($\underline{C}$-CH_3), 57.99 (OCH_3), 114.76 (CH-P), 169.9 (C=O, ester), and 204.60 ppm (C=O, alicyclic carbonyl). In the ^{31}P NMR spectrum of 15a a signal at δ = 26.34 ppm was observed. The mass spectrum of 5a showed ion peaks at m/z= [592 (M^{+2}) 11.10%, 278(Ph_3PO) 19.01%), and 256(substrate 13) 52.12%)]. Formation of compounds 15 occurred due to nucleophilic attack by the carbanion centre of the phosphoranes (6) preferentially at the electron deficient carbon-nitrogen double bond, rather than the (NH) or carbonyl group of the bifunctional camphorquinonephenylhydrazone (13), even we used 2 mole of the phosphoranes (6), to give compounds 15 (Scheme 2).

Moreover, the reaction of camphorquinone oxime (16) with alkoxyphosphoranes (6a and 6b) was investigated. Compound 16 reacted in equimolar ratio in dry boiling toluene for 8hr, to give one and the same product 19 alongwith triphenylphosphine oxide. The structure of compound 19 is corroborated by the frequency of the C=O band in the IR spectrum at 1665 cm^{-1} and absence of the = N-OH group absorption. In its ^{1}H NMR spectrum ($CDCl_3$, δ ppm) the following singals were observed at 1.01 (s, 3H, CH_3), 1.26 (s, 6H, $2CH_3$), 1.39-1.59 (m, 2H, CH_2), 1.65-1.74 (m, 2H, CH_2), 2.53 (m, H, CH) and 5.10 (s, H, CH, aromatic). In the MS of 19 an ion peak was observed at m/z= 205 [(M^{+}) 30.54%]. Reaction of the bifunctional diketone monoxime (16) with phosphonium ylides (6) proceedes *via* oxime OH group which is transformed firstly to the nitroso-compound 16A due to the migration of the oxime proton to the electron rich centre of the molecule. The nitroso-compound reacts with ylides 6 to form the reactive intermediates 18 and triphenylphosphine oxide. Compounds 18 are cyclized *via* elimination of an alcohol molecule to produce the final product (19) (Scheme 3).

Conclusion

From the above results, it could be concluded that the reaction of the active phosphacumulenes and the stabilized phosphonium ylides with camphorquinone and its monohydrazone and monooxime derivative represents a new approach to the construction of new heterocycles. Moreover, the reaction of camphorquinone with the phosphonium reagents takes place only at the carbonyl goup in position 3 and not that in position 2. This is due to the hindred nature [25] of camphorquinone carbonyl at position 3 even when excess of the phosphorus reagents is used. Furthermore, no shift for the CH_3 group in position 1 to up - field absorption was observed in the ^1H NMR spectra of the reaction products. This confirms attack by the phosphorus reagents on the carbonyl group at position 3. The difference in the nucleophilic character and reactivity of the phosphacumulenes 5a > 5b > 5c is also demonstrated in this study. Therefore, it is safe to state that the reaction courses of active phosphacumulenes and stabilized phosphonium ylides with substrates 1, 13 and 16 are rather dependent on the nature of the reactants and the reaction temperature. These processes can be considered as new and simple routes for the preparation of different ring systems, which can not be obtained by other conventional methods.

Experimental

All melting points were measured on a Gallenkamp electrothermal digital melting point apparatus. Elemental analytical data were obtained at the analytical laboratory of the National Reseach Centre. Satisfactory elemental analyses results agreed with the calculated values. The infrared spectra were recorded in KBr disks on a Jasco Fourier Transform Infrared Spectrophotometer model FT/IR-3000E. The ^1H NMR spectra were recorded in deuterated $CDCl_3$ or DMSO on JEOL JNM-EX 270 (at 270 MHz) and /or JEOL 500 AS (at 500 MHz) Spectrometer using TMS as an internal reference. ^{13}C NMR spectra were recorded on JEOL500 AS (at 125 MHz). ^{31}P NMR spectra were run on the same spectrometer using H_3PO_4 (85%) as an external reference. Mass spectra (EI-MS) were recorded at 70 e V on a Finnigan MAT SSQ 7000 Spectrometer. The reported yields are used upon pure materials isolated by column chromatogrphy on silica gel 60 (Merck).

Reaction of camphorquinone (1) with active phosphacumulene ylides (2a-c) Preparation of 3- [2,4-Diphenylimino -3- (triphenyl - λ^5- phosphanylidene) cyclobutylide-ene]- 4,7,7-trimethyl bicyclo[2.2.1]heptan-2-one (5a).

To a solution of camphorquinone (1) (0.16g, 0.001mol) in dry THF, was added dropwise with stirring at rt a solution of (N-phenyliminovinylidene) triphenylphosphorane (2a)[26] (0.75g, 0.002 mol) in 30 ml of THF. The reaction mixture was stirred for 10hr. THF was distilled off under reduced pressure, the residue was chromatographed on silica gel using pet.ether / ethyl acetate as an eluent (7:3,*v /v*), to give 5a, as yellow crystals mp = 256ºC (66 %), and triphenylphosphine oxide was isolated, too, (mp, mixed mp=151ºC.[27]

[$C_{44}H_{39}N_2OP$, 642.77]. C, 82.22; H, 6.12; N, 4.36; P, 4.82. Found: C, 82.12; H, 6.10; N, 4.16; P, 4.53.

Reaction of Compound 1 with Active Phosphacumulenes 2b and c

To a solution of compound 1 (0.16g, 0.001 mol) in 20 ml of dry toluene, was added a solution of (2-oxovinylidene) - (2b)[28] (0.60g, 0.002 mol), or (2-thioxovinylidene)-triphenyl- phosphorane (2c)[28] (0.63g, 0.002 mol) in 30 ml of dry toluene. The reaction mixture was refluxed for 12hr when 2b was used, and for 14hr in case of 2c. After the solvent has been 5b or 5c together with triphenylphosphine oxide.

3-[2,4-Dioxo-3- (triphenyl-λ^5- phosphanylidene) cyclobutylidene] -4,7,7 trimethylbicyclo [2.2.1]heptan-2-one (5b).

Eluent: n-hexane / acetone (8:2, *v/v*) was isolated as yellow crystals, m p= 274ºC (63%). Anal. Calcd for [$C_{32}H_{29}O_3P$, 492.54]. C, 78.03; H, 5.93; P, 6.29. Found: C, 78.00; H, 5.53; P, 6.13. IR (KBr, cm^{-1}): 1754 (C= O, alicyclic carbonyl), 1719 (C= O, cyclobutanedione), 1644 (P=C), and 1437 (P-Phenyl). ^1H NMR ($CDCl_3$, δ ppm): 1.13 (s, 3H, CH_3), 1.28 (s, 6H, $2CH_3$), 1.35-1.53 (m, 2H, CH_2), 1.59-1.65 (m, 2H, CH_2), 2.36 (m, H, CH), 7.65-7.93 (m, 15H, aromatics) ppm. MS: m/ z= [302 (Ph_3P=C=C=O) 12%, and 278 (Ph_3PO) 9.95%].

3-[2,4-Dithioxo -3- (triphenyl-λ^5 - phosphanylidene) cyclobutylidene]-4,7,7-trimethylbicyclo- [2.2.1]heptan-2-one (5c).

Eluent: n-hexane /acetone (7:3, *v /v*) it was produced as yellow crystals, m p= 235 ºC (66%). Anal. Calcd for [$C_{32}H_{29}OPS_2$, 524.68]. C, 73.25; H, 5.57; P, 5.90; S, 12.22. Found: C, 73.11; H, 5.21; P, 5.43; S, 12.10. IR (KBr, cm^{-1}): 1750 (C=O), 1432 (P-Phenyl), and 1130 cm^{-1} (C=S), ^1H NMR ($CDCl_3$, δ ppm): 1.14 (s, 3H, CH_3), 1.28 (s, 6H, $2CH_3$), 1.37-1.64 (m, 2H, CH_2), 1.69-1.84 (m, 2H, CH_2), 2.31 (m, H, CH), 7.64-7.83 ppm (m, 15H, aromatics). MS: m/z= 262[M^+ - (PPh_3) 42.83%, and 278 (Ph_3PO) 100%].

When the reaction of camphorquinone (1) and active phosphacumulenes 2(a-c) was carried out in (1:4 molar ratio), the same products 5(a-c) and triphenylphosphine oxide were produced.

Reaction of 3-(2-phenylhydrazono)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (13) with active phosphacumulenes (2a and b).

Camphorquinonephenylhydrazone (13) (0.26g, 0.001 mol) was added dropwise to a solution of phosphacumulenes (2a) (0.37g, 0.001 mol) or 2b (0.30g, 0.001) in dry THF (30ml), and the reaction mixture was refluxed for 10hr in case of 2a and 14hr when 2b was used. The solvent was distilled off under reduced pressure, and the residue was applied to silica gel column chromatography to give 14a, and 14b, respectively.

(4',7',7'Trimethyl)-1- (methylamino) -4- (phenylamino) -3- (triphenyl-15-phosphoranylidene)– 3'H-spiro[azetidine-2,2'-bicyclo[2.2.1] heptane]-3'-one (14a).

Eluent: acetone / pet.ether 60-80ºC (2: 8, *v / v*), as yellow crystals, m p = 130 ºC (65%). Anal. Calcd for [$C_{42}H_{40}N_3OP$, 633.76]. C, 79.60; H, 6.36; N, 6.63; P, 4.89. Found: C, 79.43; H, 6.12; N, 6.36; P, 4.55.

4',7',7'-Trimethyl)-1- (phenylamino)-3- (triphenyl -15-phosphoranylidene)-3'H,4H-spiro[aze- tidine-2,2'-bicyclo[2.2.1]heptane]-3',4-dione (14b).

Eluent: acetone / pet.ether 60-80ºC (2:8, *v / v*), as yellow crystals, mp= 145ºC (66%). Anal. Calcd for [$C_{36}H_{35}N_2O_2P$, 558.65]. C, 77.40; H, 6.31; N, 5.01; P, 5.54. Found: 77.23; H, 6.11; N, 5.43; P, 5.10. IR (KBr, cm^{-1}): 3210 (NH), 1765 (C=O, alicyclic carbonyl), 1672 (N-C=O), and 1379 cm^{-1} (P-Phenyl). ^{1}H NMR (DMSO, δ ppm): 0.98 (s, 3H, CH_3), 1.13 (s, 6H, $2CH_3$), 1.47-1.59 (m, 2H, CH_2), 1.65- 1.84 (m, 2H, CH_2), 2.62 (m, H, CH), 7.14-7.28 (m, 20H, aromatics) , and 11.86 ppm (s, H, NH, exchangeable with D_2O). ^{13}C NMR (DMSO, δ ppm):18.59 (CH_3), 20.66 ($2CH_3$), 26.11, 30.30 ($2CH_2$), 47.32 ($\underline{C}$-$(CH_3)_2$), 49.98 ($\underline{C}$-CH_3), 35.33 (CH), 144.45 (C=P), 164.46 (N-C=O), and 203.92 ppm (C=O, alicyclic). MS: m /z= [256 (substrate) 43.76%].

Reaction of 3-(hydroxyimino)-1,7,7-trimethyl bicyclo [2.2.1] heptan-2-one (16) with active phosphacumulenes (2a and 2b). Preparation of the phosphanylidenes 17a and b.

A mixture of oxime (16) (0.18g, 0.001mol), and (N-phenyliminovinylidene)-(2a)[26] (0.37g, 0.001 mol) or (2-oxovinylidene)-triphenylphosphorane (2b)[26] (0.30g, 0.001 mol) in dry toluene 30 ml was refluxed for 8hr when 2a was used and for 12hr with 2b. Toluene was distilled off and the residue was chromatographed on silica gel to give the phosphanylidenes (17a and 17b), respectively.

1,7,7- (Trimethyl - ({[(N-phenyl -2- (triphenyl -λ^5- phosphanylidene) ethanimidoyl] oxy}imino) - bicyclo[2.2.1] heptan-2-one (17a).

Eluent: pet.ether 60-80ºC, ethyl acetate (7: 3, *v/ v*) as yellow crystals, mp=105ºC (75 %), from cyclohexane. Anal.Calcd for [$C_{36}H_{35}N_2O_2P$, 558.65]. C, 77.40; H, 6.31; N, 5.01; P, 5.54. Found: C, 77.13; H, 6.13; N, 5.00; P, 5.41.

1,7,7-Trimethyl -3- ({[(triphenyl -λ^5 -phosphanylidene) acetyl] oxy}imno) bicyclo[2.2.1]heptan- 2- one (17b)

Eluent: pet.ether 60-80ºC, ethyl acetate (7: 3, *v/ v*) it was obtained as yellow crystals, mp=125ºC (65 %), from cyclohexane. Anal. Cald for [$C_{30}H_{30}NO_3P$, 483.54] C, 74.52; H, 6.25; N, 2.90; P, 6.41. Found: C, 74.32; H, 6.11; N, 2.53; P, 6.20.

^{1}H NMR ($CDCl_3$, δ ppm): 0.98 (s, 3H, CH_3), 1.24 (s, 6H, $2CH_3$), 1.32-1.57 (m, 2H, CH_2), 1.63-1.83 (m, 2H, CH_2), 2.48 (m, H, CH), 3.84 (d, H, CH=P, $^2J_{HP}$=23.9 Hz), 7.44-7.71 (m, 15H, aromatics). ^{13}C NMR ($CDCl_3$, δ ppm): 14.34(CH_3), 21.30($2CH_3$), 22.72, 29.72 ($2CH_2$), 44.53(CH), 47.64 ($\underline{C}$-$(CH_3)_2$),

54.21(C-CH_3), 57.52 (C=P), 156.23 (C=P), 166.23 (C=N), 176.12 (N-C=O), 202.51(C=O, alicyclic carbonyl). MS: m /z = [221 (M^+- PPh_3) 9.65%], 181 (M^+ – ylide) 96.71%].

Reaction of camphorquinone 1 with the stabilized phosphonium ylide (6a). Prepation of the 3 products (8, 10, and 12).

A mixture of 1 (0.16g, 0.001 mol) and methoxycarbonyl methylenetriphenyl phosphorane (6a)[29] (0.67g, 0.002 mol) was boiled in dry toluene (30 ml) for 8hr. The solvent was distilled off and the residue was chromatographed on silica gel using pet. ether 60-80 ºC / acetone as an eluent, affording 3 adducts (8, 10, and 12) respectively, alongwith triphenylphosphine and triphenylphosphine oxide.

Methyl-4,7,7-trimethyl-2',2',2''triphenyl -3-oxospiro[bicyclo[2.2.1] heptane-2,4'-[1,2]oxa- phosphetane]-3'-carboxylate (8)

Eluent: pet.ether 60-80 ºC / acetone (8: 2, *v/v*) it was obtained as yellow crystals (40 %). Anal. Calcd for [$C_{31}H_{33}O_4P$, 500.57] C, 74.38; H, 6.64; P, 6.19. Found: C, 74.21; H, 6.30; P, 6.11.

Dimethyl-2-(4,7,7-trimetyl-3- oxobicyclo [2.2.1]hept-2-yl-3- (triphenyl-λ^5-phosphanylidene)-butanedioate (10)

Eluent: pet.ether 60-80 ºC / acetone (7: 3, *v/v*) it was obtained as yellow crystals (25 %). Anal. Calcd for [$C_{34}H_{37}O_5P$, 556.63] C, 73.36; H, 6.70; P, 5.56. Found: C, 73.16; H, 6.32; P, 5.31

Methyl-1,11,11-trimethyl-4-oxo-3-oxatricyclo[6.2.1.$0^{2,7}$]undeca-2(7),5-diene-6-carb-oxylate (12).

Eluent: pet.ether 60-80 ºC / acetone (6: 4, *v/v*) it was obtained as yellow crystals (15%) Anal Calcd for $C_{15}H_{18}O_4$, 262.30] C, 68.68; H, 6.92. Found: C, 68.31; H, 6.63.

Reaction of camphorquinonephenylhydrazone (13) with stabilized phosphonium ylides (6a and b).

Camphorquinonephenylhydrazone (13) (0.26g, 0.001 mol) was added to a solution of methoxycarbonyl- (6a)[29] (0.33g, 0.001 mol) or ethoxycarbonyl-methylenetriphenylphospho- rane (6b)[29] (0.34g, 0.001 mol) in dry toluene (30ml), and the reaction mixture was refluxed for 10hr in case of 6a and 12hr when 6b was used. The solvent was distilled off under reduced pressure; the residue was applied to silica gel column chromatography to afford compounds 15a and 15b, respectively.

4',7',7'-Trimethyl-methyl 2,2,2-triphenyl-1- (methylamino)-3'-oxospiro[1,2-azaphophetidine-4, 2'-bicyclo[2.2.1]heptane]-3-carboxylate (15a).

Eluent: acetone / pet.ether 60-80 ºC (2:8, *v / v*), as yellow crystals, mp=166 ºC (65%). Anal. Calcd for [$C_{37}H_{39}N_2O_3P$, 590.69]. C, 75.23; H, 6.65; N, 4.74; P, 5.24. Found: C, 75.01; H, 6.32; N, 4.63; P, 5.13.

4',7',7'-Trimethyl- ethyl2,2,2-triphenyl -1- (methylamino)-3'-oxospiro[1,2-azaphosphetidine- 4,2'-bicyclo[2,2,1]heptane]-3-carboxylate (15b).

Eluent: acetone / pet.ether 60-80ºC (3:7 v/v), yellow crystals, mp=135 ºC (67%). Anal. Calcd for [$C_{38}H_{41}N_2O_3P$, 604.72] C, 75.47; H, 6.83; N, 4.63; P, 5.12. Found: C, 75.26; H, 6.44; N, 4.31; P, 5.00. IR (KBr, cm^{-1}): 3100 (NH), 1713 (C=O, alicyclic carbonyl), 1692 (N-C=O), 1492 cm^{-1} (P-Phenyl). ^{1}H NMR (CDCl,δ ppm): 0.89 (s, 3H, CH_3), 1.11 (s, 6H, $2CH_3$), 1.29 (t, 3H, $\underline{CH_3}$ CH_2), 1.36-1.48 (m, 2H, CH_2), 1.53-1.72 (m, 2H, CH_2), 2.25 (m, H, CH), 2.84 (d, H, CH-P), 4.21 (q, 2H, CH_3 $\underline{CH_2}$), 6.56-6.69 (m, 5H, aromatic), 7.13-7.45 (m, 15H, aromatic), 11.54 ppm (s, H, NH, exchangeable with D_2O). MS: m/z= [342(M^+-PPh_3) 5.34%, 262(PPh_3)56.43%, and 256 (substrate 13) 85.22%].

Reaction of camphorquinone monooxime (16) with stabilized phosphonium ylides (6a and b).

Camphorquinone monooxime (16) (0.18g, 0.001 mol) was added to a solution of methoxycarbonyl- (6a) (0.37g, 0.001 mol) or ethoxycarbonyl-methylenetriphenylphosphorane (6b) (0.34g, 0.001 mol) in dry toluene (30ml), and the reaction mixture was refluxed for 8hr. The solvent was distilled off under reduced pressure and the residue was applied to silica gel column chromatography using pet.ether 60-80 ºC/ethyl acetate as eluent (6:4, v/v) to afford compound 19, and triphenylphosphine oxide.

1,11,11-trimethyl-3-oxa-6-azatricyclo [6.2.1.0^{2,7}] undeca-2 (7), 5-dien-4-one (19),

It was isolated as colorless crystals, mp=115ºC (55%). Anal. Calcd for [$C_{12}H_{15}NO_2$, 205.25] C, 70.22; H, 7.37; N, 6.82. Found: C, 70.13; H, 7.21; N,6.53.

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كيمياء ايليدات الفوسفور : تفاعل مشتقات كومفركينون مع ايليدات الفوسفونيوم المتراكمه النشطه وايليدات الفوسفونيوم الثابته

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فى هذا البحث تم دراسة تفاعلات مركبات الكومفركينون (1) ، أحادى فينيل الهيدرازون (13) وأحادى الاوكزيم (16) مع كواشف ايليدات الفوسفونيوم النشطه والتى نتج عنها مركبات فوسفانيليدين سيكلوبيوتيليدين (5) ، آزيتيدين ثنائى الحلقه هيبتانونوز (14) وفوسفانيليدينز (17) بالتتابع . وعلى صعيد آخر ، تم دراسة تفاعلات ايليدات الفوسفونيوم الثابته (6) مع المركبات السابقه 1، 13 ، 16 ، لتعطى اوكسافوسفيتان (8) ، فوسفانيليدين (10) ، اوكساتريسيكلوايندكادين (12) ، آزوفوسفيتدينز (15) وآزوتريسيكلوايندكادينونز (19) .

وقد تأيدت التركيبات البنائيه المقترحه للنواتج الجديده بواسطة الاساليب التحليليه و الطيفيه .