

Venkatapuram Padmavathi* [a], Tippireddy Venkat Ramana Reddy [b],
Kamireddy Audishesha Reddy^b and Dandu Bhaskar Reddy^a

[a] Department of Chemistry, Sri Venkateswara University, Tirupati -517 502, India
[b] Chemical Laboratory, SPROB, SHAR Centre / ISRO / DOS, Sriharikota -524 121, India
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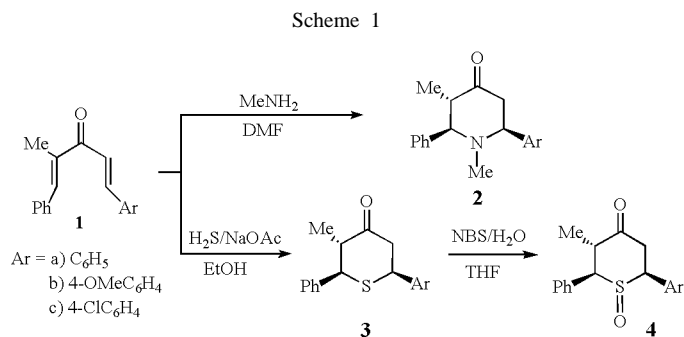
A number of annelated heterocyclic indene derivatives having 1,2,3-selena/thiadiazole and 2*H*-1,2,3-diazaphosphole rings have been synthesized by exploiting the α -ketomethylene functionality in some novel 1-methyl-piperidin-4-ones and 1-oxo-tetrahydrothiopyran-4-ones and were characterized by their physical and spectral data.

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Molecules with heteroaromatic rings are widely distributed in nature. Indeed a number of heterocyclic compounds containing nitrogen, sulfur and other heteroatoms exhibit a variety of biological activity. The concept of isosteric exchange is a tool for modifying the activity of biologically important molecules. One such isosteric pair constitutes sulfur and selenium. Recently a great deal of interest is envisaged in annelated heterocycles. In fact, some bicyclic annelated 1,2,3-selena/thiadiazoles and diazaphospholes were found to be potential bioactive agents [1]. Although, we have been actively involved for quite some time in the synthesis of a variety of heterocycles, in the recent past, however, we have diverted our attention to annelated heterocycles, particularly 1,2,3-selena/thiadiazole rings fused to carbocyclic [2] and heterocyclic [3] systems. The attraction to this is multifaceted with the main reason being that this process had received scant attention in the literature and in addition we wished to extend this methodology to the synthesis of a wide range of annelated heterocycles. Therefore, in continuation of our efforts herein we report some novel 1,2,3-selena/thiadiazoles and 2*H*-1,2,3-diazaphospholes fused to 1-methyl-piperidin-4-ones and 1-oxo-tetrahydrothiopyran-4-ones.

The precursor ketones 1,3-dimethyl-2-phenyl-6-aryl-piperidin-4-ones (**2**), 3-methyl-2-phenyl-6-aryl-tetrahydrothiopyran-4-ones (**3**) and 3-methyl-1-oxo-2-phenyl-6-aryltetrahydrothiopyran-4-ones (**4**) were prepared from 2-methyl-1-phenyl-5-aryl-1,4-pentadien-3-ones (**1**). The condensation of **1** with methylamine in dimethylformamide [4] gave **2**. Compound **3** was prepared by passing H₂S into a refluxing solution of **1** in ethanol in presence of sodium acetate (2 fold) for 15-18 hours [5] and S-oxidation of **3** with *N*-bromosuccinimide [6] resulted **4**. (see Scheme 1 and Table 1). The sulphoxides were prepared generally from sulphides by a variety of reagents as single or mixture of isomers [7]. However, it was observed that, *N*-bromosuccinimide in tetrahydrofuran at room temperature yielded sulphoxides in high yield. In all these cases, although isomeric products could be possible, the isomers (2*R*,3*S*,6*S*)-1-methyl-2,6-diaryl-3-methylpiperidin-4-one

(**2**), (2*R*,3*S*,6*S*)-2,6-diaryl-3-methyltetrahydrothiopyran-4-one (**3**) and (2*R*,3*S*,6*S*)-1-oxo-2,6-diaryl-3-methyl-tetrahydrothiopyran-4-one (**4**) were obtained predominantly. The conformations of these compounds were further ascertained on the basis of their NMR data explained below [5,8].



The Infrared spectra (ν , cm⁻¹) of **2** showed medium-to-strong bands in the region 2765-2775 (N-Me), 1720-1725 (C=O) and at 1040-1055 (S=O), 1710-1720 (C=O) for **4**. In the ¹H NMR spectra (δ , ppm and *J*, Hz) of **2**, the proton at C₂ displayed a doublet between 3.00-3.06 (*J* \approx 10.3) owing to AB splitting pattern, while proton at C₃ exhibited a quintet or multiplet in the region 2.78-2.93. The observed coupling constant *J* = 10.3 Hz certainly suggest that the phenyl group and methyl group are in equatorial positions. The C₅ protons showed a doublet of doublet around 2.55-2.61 (*J* \approx 14.8, 3.3) and a triplet between 2.80-2.94, whereas the proton at C₆ exhibited a doublet of doublet in the region 3.39-3.46 (*J* \approx 14.5, 3.0) pertaining to an ABX splitting pattern. The coupling constants *J* = 14.5 & 3.0 Hz which are typical for vicinal couplings *J*_{anti} and *J*_{gauche} in the chair conformation indicate that the proton at C₆ is in axial position. The ¹H NMR spectra of **3** is in accordance with reported values [5]. A similar splitting pattern was observed for **4**, whose protons showed resonance signals around 3.82-3.87 (d, *J* \approx 10.8, C₂), 3.14-3.35 (m, C₃ and C_{5-ax}), 3.04-3.08 (dd, *J* \approx 14.3, 3.6, C_{5-eq}) and 4.08-4.18 (dd, *J* \approx 14.6, 3.5, C₆). Thus **2**, **3** and **4** exist in

Table 1
Physical Data of Compounds **2**, **3**, **4** and **7** – **12**

Compd. No	Yield (%)	M. P. (°C)	Mol. Formula (Mol. Wt.)	Calcd. (Found) (%)		
				C	H	N
2a	52	131-132	(lit. [14] mp 130-131)			
2b	45	145-147	C ₂₀ H ₂₃ NO ₂ (309.4)	77.64 (77.83)	7.49 (7.44)	4.53 (4.42)
2c	48	163-165	C ₁₉ H ₂₀ ClNO (313.8)	72.72 (72.86)	6.42 (6.50)	4.46 (4.35)
3a	30	124-125	(lit. [5] mp 123-125)			
3b	25	142-144	(lit. [5] mp 145-146)			
3c	28	139-140	(lit. [5] mp 137-138)			
4a	88	185-187	C ₁₈ H ₁₈ O ₂ S (298.4)	72.45 (72.57)	6.08 (6.15)	-
4b	82	171-173	C ₁₉ H ₂₀ O ₃ S (328.4)	69.48 (69.30)	6.14 (6.05)	-
4c	80	198-200	C ₁₈ H ₁₇ ClO ₂ S (332.9)	64.95 (65.11)	5.15 (5.23)	-
7a	55	158-160	C ₁₉ H ₁₉ N ₃ Se (368.3)	61.96 (61.85)	5.20 (5.26)	11.41 (11.28)
7b	58	150-152	C ₂₀ H ₂₁ N ₃ Ose (398.4)	60.30 (60.45)	5.31 (5.38)	10.55 (10.40)
7c	50	171-173	C ₁₉ H ₁₈ ClN ₃ Se (402.8)	56.66 (56.49)	4.50 (4.61)	10.43 (10.60)
8a	60	168-170	C ₁₈ H ₁₆ N ₂ OSSe (387.4)	55.81 (55.75)	4.16 (4.10)	7.23 (7.13)
8b	55	180-182	C ₁₉ H ₁₈ N ₂ O ₂ SSe (417.4)	54.67 (54.58)	4.35 (4.44)	6.71 (6.59)
8c	56	210-212	C ₁₈ H ₁₅ ClN ₂ OSSe (421.8)	51.25 (51.39)	3.58 (3.65)	6.64 (6.55)
9a	62	156-158	C ₁₉ H ₁₉ N ₃ S (321.4)	70.99 (71.16)	5.96 (6.03)	13.07 (12.83)
9b	60	164-166	C ₂₀ H ₂₁ N ₃ OS (351.5)	68.35 (68.56)	6.02 (6.13)	11.96 (11.79)
9c	57	180-182	C ₁₉ H ₁₈ ClN ₃ S (355.9)	64.12 (63.92)	5.10 (5.18)	11.81 (11.62)
10a	54	200-202	C ₁₈ H ₁₆ N ₂ OS ₂ (340.5)	63.50 (63.63)	4.74 (4.80)	8.23 (8.09)
10b	50	186-188	C ₁₉ H ₁₈ N ₂ O ₂ S ₂ (370.5)	61.59 (61.41)	4.90 (4.82)	7.56 (7.69)
10c	52	190-192	C ₁₈ H ₁₅ ClN ₂ OS ₂ (374.9)	57.67 (57.83)	4.03 (4.10)	7.47 (7.30)
11a	60	175-177	C ₂₅ H ₂₄ N ₃ P (397.5)	75.55 (75.33)	6.09 (6.00)	10.57 (10.48)
11b	56	161-163	C ₂₆ H ₂₆ N ₃ OP (427.5)	73.58 (73.30)	6.13 (6.24)	9.83 (9.71)
11c	53	158-160	C ₂₅ H ₂₃ ClN ₃ P (431.9)	69.52 (69.29)	5.37 (5.25)	9.73 (9.51)
12a	59	182-184	C ₂₄ H ₂₁ N ₂ OPS (416.5)	69.21 (69.42)	5.08 (5.13)	6.73 (6.84)
12b	57	193-195	C ₂₅ H ₂₃ N ₂ O ₂ PS (446.5)	67.25 (67.03)	5.19 (5.11)	6.27 (6.18)
12c	54	218-220	C ₂₄ H ₂₀ ClN ₂ OPS (450.9)	63.93 (64.13)	4.47 (4.53)	6.21 (6.06)

the preferred chair conformation with *cis*-orientation at C₂, C₆ and *trans* at C₂, C₃ (Figure -1).

However, the N-methyl orientation in **2** can be in equatorial or axial position as shown in figure-1. The equatorial N-Me is more preferred since the substituents at 1 and 3 positions would be in the stable 1,3-*cis*-orientation [9]. On the other hand, the oxygen atom on sulfur in **4** should also

occupy either axial or equatorial positions, but the axial orientation is preferred as such a disposition on the sulfur in a six membered ring is the energetically favoured conformation [10]. Thus, the thermodynamically more stable isomer was preferred in each case, among the possible stereoisomers. The δ_C values obtained in their ¹³C NMR spectra are shown in Table 2.

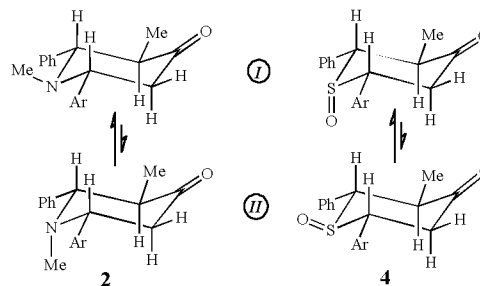


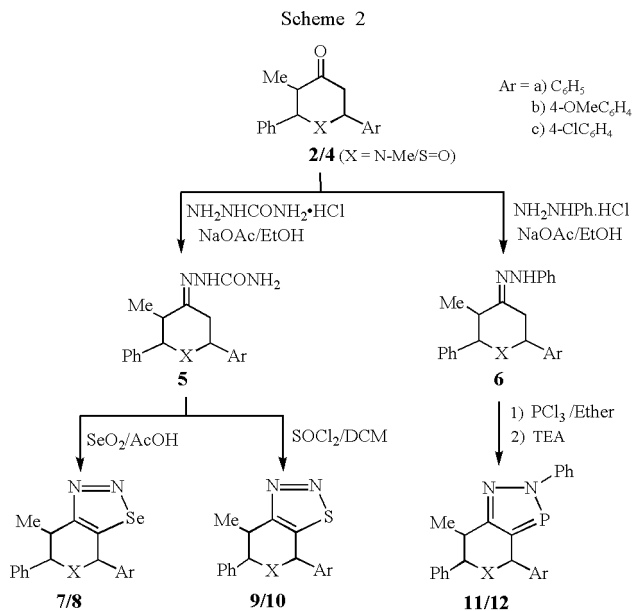
Figure 1

The presence of α -ketomethylene functionality in these 1-hetera-4-cyclohexanones served as building block for the development of annelated heterocycles. Compounds **2** and **4**, on reaction with semicarbazide and phenylhydrazine, gave their respective semicarbazones (**5**) and phenylhydrazones (**6**). The oxidative cyclization of the semicarbazones (**5**) with selenium dioxide in acetic acid at 60-70 °C [11] furnished 5,7-dimethyl-4-aryl-6-phenyl-4,5,6,7-tetrahydro-3-selena-1,2,5-triazaindene (**7**) and 7-methyl-4-aryl-6-phenyl-6,7-dihydro-4*H*-5-thia-3-selena-1,2-diazaindene-5-oxide (**8**). However, the Hurd-Moori reaction process with excess thionylchloride in dichloromethane at 0 °C [12] produced 5,7-dimethyl-4-aryl-6-phenyl-4,5,6,7-tetrahydro-3-thia-1,2,5-triazaindene (**9**) and 7-methyl-4-aryl-6-phenyl-6,7-dihydro-4*H*-3,5-dithia-1,2-diazaindene-5-oxide (**10**). On the other hand, when **6** was subjected to the cyclization process with phosphorous trichloride in dry ether in the presence of triethylamine at -5 to -10 °C [13] 5,7-dimethyl-4-aryl-2,6-diphenyl-4,5,6,7-tetrahydro-2*H*-1,2,5-triaza-3-phosphaindene (**11**) and 7-methyl-4-aryl-2,6-diphenyl-2,4,6,7-tetrahydro-5-thia-2*H*-1,2-diaza-3-phosphaindene-5-oxide (**12**) resulted.

Compound **5** displayed bands between 3220-3440 (*NHCO* and *CONH*₂), 1685-1695 and 1555-1570 (*CONH*₂) and 1635-1650 (*C=N*) for semicarbazone moiety, while bands in the region 3280-3300 (*NH*) and 1590-1605 (*C=N*) are due to the phenylhydrazone moiety of **6**. The absence of bands due to semicarbazone unit and the presence of bands at 1430-1455 (*N=N*) and 680-735 (*C-S/Se*) indicate that cyclization indeed has taken place in **7** - **10**. Similarly, the absence of *NH* band and the presence of bands around 1580-1600 (*C=N*) confirmed the formation of diazaphospholes, **11** and **12**. The ¹H NMR spectra of **7** - **12** differ very much from that of **2** and **4**. Three different

Table 2
NMR Spectral Data of Compounds 2, 4 and 7 – 12

No.	¹ H NMR (δ, ppm)	¹³ C NMR (δ, ppm)
2a	0.78 (d, 3H, CH ₃ , <i>J</i> =6.6 Hz), 1.75 (s, 1H, N-CH ₃), 2.55 (dd, 1H, H _{eq} -5, <i>J</i> = 14.8, 3.3 Hz), 2.82 - 2.93 (m, 2H, H _{ax} -5 & H-3), 3.01 (d, 1H, H-2, <i>J</i> =10.3 Hz) 3.43 (dd, 1H, H-6, <i>J</i> =14.5, 3.5 Hz), 7.24 -7.45 (m, 10H, Ar-H).	10.35 (CH ₃), 41.15 (NCH ₃), 49.52 (C ₅), 51.21 (C ₃), 70.26 (C ₆), 77.88 (C ₂), 208.53 (C ₄).
2b	0.84 (d, 3H, CH ₃ , <i>J</i> =6.8 Hz), 1.73 (s, 1H, N-CH ₃), 2.61 (dd, 1H, H _{eq} -5, <i>J</i> = 14.5, 3.4 Hz), 2.81 (q, 1H, H-3), 2.94 (t, 1H, H _{ax} -5), 3.08 (d, 1H, H-2, <i>J</i> =10.1 Hz) 3.49 (dd, 1H, H-6, <i>J</i> =14.2, 3.8 Hz), 3.80 (s, 3H, OCH ₃), 6.85-7.38 (m, 9H, Ar-H).	10.80 (CH ₃), 41.22 (NCH ₃), 49.18 (C ₅), 51.67 (C ₃), 55.34 (OCH ₃), 70.63 (C ₆), 78.02 (C ₂), 207.36 (C ₄).
2c	0.82 (d, 3H, CH ₃ , <i>J</i> =6.6 Hz), 1.76 (s, 1H, N-CH ₃), 2.56 (dd, 1H, H _{eq} -5, <i>J</i> = 14.7, 3.3 Hz), 2.80-2.91 (m, 2H, H-3 & H _{ax} -5), 3.12 (d, 1H, H-2, <i>J</i> =10.2 Hz) 3.56 (dd, 1H, H-6, <i>J</i> =14.4, 3.1 Hz), 7.06-7.43 (m, 9H, Ar-H).	10.44 (CH ₃), 41.08 (NCH ₃), 49.35 (C ₅), 51.82 (C ₃), 70.38 (C ₆), 77.64 (C ₂), 208.13 (C ₄).
4a	1.04 (d, 3H, CH ₃ , <i>J</i> =6.9 Hz), 3.08 (dd, 1H, H _{eq} -5, <i>J</i> = 14.3, 3.8 Hz), 3.21 (q, 1H, H-3), 3.32 (t, 1H, H _{ax} -5), 4.12 (d, 1H, H-2, <i>J</i> =9.4 Hz) 4.32 (dd, 1H, H-6, <i>J</i> =14.5, 3.6 Hz), 7.09-7.32 (m, 10H, Ar-H).	12.48 (CH ₃), 50.87 (C ₃), 52.92 (C ₅), 60.70 (C ₆), 66.88 (C ₂), 209.75 (C ₄).
4b	1.01 (d, 3H, CH ₃ , <i>J</i> =6.6 Hz), 2.97 (dd, 1H, H _{eq} -5, <i>J</i> = 14.2, 3.6 Hz), 3.14 -3.30 (m, 2H, H-3 & H _{ax} -5), 3.73 (s, 3H, OCH ₃), 4.07 (d, 1H, H-2, <i>J</i> =9.2 Hz) 4.40 (dd, 1H, H-6, <i>J</i> =14.7, 3.8 Hz), 6.74-7.31 (m, 9H, Ar-H).	12.65 (CH ₃), 50.65 (C ₃), 52.49 (C ₅), 54.99 (OCH ₃), 61.85 (C ₆), 66.32 (C ₂), 208.98 (C ₄).
4c	1.08 (d, 3H, CH ₃ , <i>J</i> =6.8 Hz), 3.04 (dd, 1H, H _{eq} -5, <i>J</i> = 14.4, 3.7 Hz), 3.16 -3.34 (m, 2H, H-3 & H _{ax} -5), 4.10 (d, 1H, H-2, <i>J</i> =9.2 Hz) 4.43 (dd, 1H, H-6, <i>J</i> =14.5, 3.6 Hz), 6.85-7.30 (m, 9H, Ar-H).	12.60 (CH ₃), 50.53 (C ₃), 52.73 (C ₅), 61.13 (C ₆), 65.92 (C ₂), 210.02 (C ₄).
7a	1.39 (d, 3H, CH ₃ , <i>J</i> =6.6 Hz), 1.89 (s, 3H, NCH ₃), 3.25 (d, 1H, H-6, <i>J</i> =9.6 Hz), 3.62-3.67 (m, 1H, H-7), 4.57 (s, 1H, H-4), 7.23-7.44 (m, 10H, Ar-H).	17.58 (CH ₃), 39.45 (C ₇), 41.60 (NCH ₃), 70.14 (C ₄), 74.61 (C ₆), 143.50 (C ₉), 152.56 (C ₈).
7b	1.33 (d, 3H, CH ₃ , <i>J</i> =6.8 Hz), 1.91 (s, 3H, NCH ₃), 3.32 (d, 1H, H-6, <i>J</i> =9.5 Hz), 3.60-3.66 (m, 1H, H-7), 3.83 (s, 3H, OCH ₃), 4.48 (s, 1H, H-4), 6.91-7.39 (m, 9H, Ar-H).	17.40 (CH ₃), 40.07 (C ₇), 41.68 (NCH ₃), 55.26 (OCH ₃), 69.73 (C ₄), 74.22 (C ₆), 145.03 (C ₉), 151.92 (C ₈).
7c	1.42 (d, 3H, CH ₃ , <i>J</i> =6.6 Hz), 1.86 (s, 3H, NCH ₃), 3.20 (d, 1H, H-6, <i>J</i> =9.5 Hz), 3.57-3.64 (m, 1H, H-7), 4.51 (s, 1H, H-4), 7.02-7.41 (m, 9H, Ar-H).	17.32 (CH ₃), 39.71 (C ₇), 41.77 (NCH ₃), 69.48 (C ₄), 75.06 (C ₆), 142.62 (C ₉), 151.72 (C ₈).
8a	1.45 (d, 3H, CH ₃ , <i>J</i> =6.8 Hz), 3.50-3.58 (m, 1H, H-7), 4.20 (d, 1H, H-6, <i>J</i> =9.0 Hz), 4.60 (s, 1H, H-4), 7.11-7.36 (m, 10H, Ar-H).	17.45 (CH ₃), 40.73 (C ₇), 59.21 (C ₄), 65.05 (C ₆), 144.23 (C ₉), 151.43 (C ₈).
8b	1.38 (d, 3H, CH ₃ , <i>J</i> =6.5 Hz), 3.46-3.52 (m, 1H, H-7), 3.78 (s, 3H, OCH ₃), 4.26 (d, 1H, H-6, <i>J</i> =9.2 Hz), 4.66 (s, 1H, H-4), 6.80-7.28 (m, 9H, Ar-H).	17.36 (CH ₃), 41.32 (C ₇), 54.86 (OCH ₃), 60.44 (C ₄), 65.56 (C ₆), 143.02 (C ₉), 153.08 (C ₈).
8c	1.40 (d, 3H, CH ₃ , <i>J</i> =6.6 Hz), 3.52-3.59 (m, 1H, H-7), 4.21 (d, 1H, H-6, <i>J</i> =9.0 Hz), 4.75 (s, 1H, H-4), 6.84-7.32 (m, 9H, Ar-H).	17.52 (CH ₃), 40.98 (C ₇), 60.85 (C ₄), 64.88 (C ₆), 145.11 (C ₉), 152.75 (C ₈).
9a	1.25 (d, 3H, CH ₃ , <i>J</i> =6.5 Hz), 1.83 (s, 3H, NCH ₃), 3.18 (d, 1H, H-6, <i>J</i> =9.8 Hz), 3.55-3.62 (m, 1H, H-7), 4.51 (s, 1H, H-4), 7.25-7.51 (m, 10H, Ar-H).	16.73 (CH ₃), 40.22 (C ₇), 41.53 (NCH ₃), 69.86 (C ₄), 74.02 (C ₆), 140.42 (C ₉), 151.56 (C ₈).
9b	1.22 (d, 3H, CH ₃ , <i>J</i> =6.6 Hz), 1.88 (s, 3H, NCH ₃), 3.23 (d, 1H, H-6, <i>J</i> =9.5 Hz), 3.48-3.56 (m, 1H, H-7), 3.77 (s, 3H, OCH ₃), 4.32 (s, 1H, H-4), 6.80-7.37 (m, 9H, Ar-H).	16.58 (CH ₃), 39.29 (C ₇), 41.43 (NCH ₃), 56.12 (OCH ₃), 70.23 (C ₄), 74.61 (C ₆), 138.85 (C ₉), 150.83 (C ₈).
9c	1.29 (d, 3H, CH ₃ , <i>J</i> =6.5 Hz), 1.85 (s, 3H, NCH ₃), 3.11 (d, 1H, H-6, <i>J</i> =9.7 Hz), 3.54-3.60 (m, 1H, H-7), 4.40 (s, 1H, H-4), 6.96-7.42 (m, 9H, Ar-H).	17.04 (CH ₃), 39.86 (C ₇), 41.61 (NCH ₃), 69.92 (C ₄), 74.73 (C ₆), 141.05 (C ₉), 150.27 (C ₈).
10a	1.31 (d, 3H, CH ₃ , <i>J</i> =6.6 Hz), 3.45-3.52 (m, 1H, H-7), 4.28 (d, 1H, H-6, <i>J</i> =9.0 Hz), 4.73 (s, 1H, H-4), 7.18-7.44 (m, 10H, Ar-H).	17.01 (CH ₃), 39.86 (C ₇), 61.83 (C ₄), 67.13 (C ₆), 141.13 (C ₉), 150.21 (C ₈).
10b	1.37 (d, 3H, CH ₃ , <i>J</i> =6.7 Hz), 3.41-3.47 (m, 1H, H-7), 3.74 (s, 3H, OCH ₃), 4.20 (d, 1H, H-6, <i>J</i> =9.2 Hz), 4.82 (s, 1H, H-4), 6.92-7.35 (m, 9H, Ar-H).	16.72 (CH ₃), 41.02 (C ₇), 55.80 (OCH ₃), 61.35 (C ₄), 66.48 (C ₆), 139.75 (C ₉), 151.14 (C ₈).
10c	1.28 (d, 3H, CH ₃ , <i>J</i> =6.5 Hz), 3.38-3.44 (m, 1H, H-7), 4.36 (d, 1H, H-6, <i>J</i> =8.9 Hz), 4.70 (s, 1H, H-4), 6.88-7.32 (m, 9H, Ar-H).	17.35 (CH ₃), 40.71 (C ₇), 61.02 (C ₄), 66.64 (C ₆), 140.73 (C ₉), 150.83 (C ₈).
11a	1.31 (d, 3H, CH ₃ , <i>J</i> =6.4 Hz), 1.85 (s, 3H, NCH ₃), 3.20 (d, 1H, H-6, <i>J</i> =9.6 Hz), 3.51-3.58 (m, 1H, H-7), 4.32 (s, 1H, H-4), 7.20-7.46 (m, 15H, Ar-H).	16.95 (CH ₃), 38.73 (C ₇), 41.67 (NCH ₃), 67.93 (C ₄), 75.22 (C ₆), 148.35 (C ₈), 166.79 (C ₉ , <i>J</i> _{CP} =52 Hz).
11b	1.35 (d, 3H, CH ₃ , <i>J</i> =6.6 Hz), 1.78 (s, 3H, NCH ₃), 3.25 (d, 1H, H-6, <i>J</i> =9.7 Hz), 3.45-3.50 (m, 1H, H-7), 3.72 (s, 3H, OCH ₃), 4.24 (s, 1H, H-4), 7.06-7.42 (m, 14H, Ar-H).	17.14 (CH ₃), 39.31 (C ₇), 41.75 (NCH ₃), 55.62 (OCH ₃), 67.34 (C ₄), 74.86 (C ₆), 149.02 (C ₈), 164.55 (C ₉ , <i>J</i> _{CP} =53 Hz).
11c	1.33 (d, 3H, CH ₃ , <i>J</i> =6.4 Hz), 1.83 (s, 3H, NCH ₃), 3.28 (d, 1H, H-6, <i>J</i> =9.8 Hz), 3.44-3.49 (m, 1H, H-7), 4.35 (s, 1H, H-4), 6.92-7.40 (m, 14H, Ar-H).	16.78 (CH ₃), 39.38 (C ₇), 41.72 (NCH ₃), 66.88 (C ₄), 75.50 (C ₆), 148.27 (C ₈), 167.32 (C ₉ , <i>J</i> _{CP} =50 Hz).
12a	1.36 (d, 3H, CH ₃ , <i>J</i> =6.6 Hz), 3.46-3.52 (m, 1H, H-7), 4.32 (d, 1H, H-6, <i>J</i> =9.2 Hz), 4.72 (s, 1H, H-4), 7.10-7.43 (m, 15H, Ar-H).	17.62 (CH ₃), 40.92 (C ₇), 60.84 (C ₄), 67.18 (C ₆), 149.23 (C ₈), 164.95 (C ₉ , <i>J</i> _{CP} =54 Hz).
12b	1.30 (d, 3H, CH ₃ , <i>J</i> =6.5 Hz), 3.50-3.56 (m, 1H, H-7), 3.70 (s, 3H, OCH ₃), 4.25 (d, 1H, H-6, <i>J</i> =9.0 Hz), 4.67 (s, 1H, H-4), 6.98-7.42 (m, 14H, Ar-H).	17.03 (CH ₃), 41.37 (C ₇), 55.83 (OCH ₃), 61.56 (C ₄), 66.94 (C ₆), 147.54 (C ₈), 166.87 (C ₉ , <i>J</i> _{CP} =52 Hz).
12c	1.32 (d, 3H, CH ₃ , <i>J</i> =6.7 Hz), 3.43-3.50 (m, 1H, H-7), 4.21 (d, 1H, H-6, <i>J</i> =9.0 Hz), 4.80 (s, 1H, H-4), 6.95-7.40 (m, 14H, Ar-H).	17.75 (CH ₃), 41.03 (C ₇), 61.32 (C ₄), 67.54 (C ₆), 148.58 (C ₈), 163.27 (C ₉ , <i>J</i> _{CP} =53 Hz).



sets of signals were observed for all the methine protons. In compounds **7**, **9** and **11**, a doublet around 3.17–3.31 ($J \approx 9.5$) was attributed to proton at C₆, a multiplet between 3.44 – 3.67 was due to proton at C₇ and a singlet in the downfield region 4.40–4.57 was assigned to a proton at C₄. Similarly, in the spectra of **8**, **10** and **12**, the δ_{H} values in the regions 4.21–4.36 (d, $J \approx 9.3$), 3.38–3.59 (m) and 4.70–4.88 (s) were due to the protons at C₆, C₇ and C₄ respectively. Thus based on ¹H NMR data, the two aryl substituents at C₄ and C₆, the methyl at C₇ and N-Me/S=O groups were in the preferred equatorial positions of the half-chair conformation of heteracyclohexene moiety as in **2** and **4**. Furthermore, the 1,2,3-selenadiazole/thiadiazole/diazaphosphole ring would also be almost in the average plane as that of the heteracyclohexene moiety according to the Drieding model (Figure 2). The ¹³C NMR spectral data of these are given in Table 2. The ³¹P NMR spectra of **11** and **12** displayed a signal between –205 and –210 ppm due to the dicoordinated phosphorous in evidence of the 2*H*-diazaphosphole ring formation.

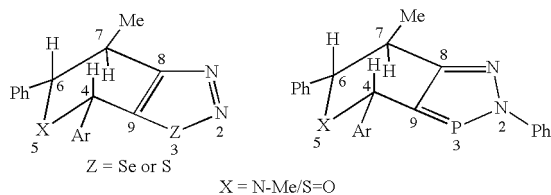


Figure 2

EXPERIMENTAL

Melting Points were determined on a Veego Scientific PMP-DM equipment and are uncorrected. Purity of the compounds

was checked by TLC using silica gel 'G' (Merck) and ethyl acetate – hexane, 1: 4 as eluents. Elemental analyses were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were plotted on Perkin-Elmer 1600 series FT-IR instrument using KBr discs and wave numbers were in cm⁻¹. NMR spectra were recorded on a Bruker DPX 300 spectrometer in CDCl₃ solution. The chemical shifts (δ) were measured in ppm using TMS as internal standard for ¹H and ¹³C NMR and 85% Phosphoric acid (external) for ³¹P NMR.

The unsaturated ketones, 2-methyl-1-phenyl-5-aryl-1,4-pentadien-3-one (**1**) and (2*R*,3*S*,6*S*)-2,6-diaryl-3-methyltetrahydrothiopyran-4-one (**3**) were prepared according to the literature procedures [5].

General Procedure.

1,3-Dimethyl-2-phenyl-6-aryl-piperidin-4-ones (**2**).

To a well stirred solution of **1** (15 mmoles) in dimethylformamide (30 mL), 40% aqueous methylamine (20 mmoles) was added during a period of 30 minutes and stirring was continued for 25-30 hours at ambient temperature. The reaction mixture was then poured onto crushed ice and the separated solid was collected by filtration. The crude product was triturated with ethanol, filtered, dried and recrystallised from ethanol.

General Procedure.

3-Methyl-1-oxo-2-phenyl-6-aryl-tetrahydrothiopyran-4-ones (**4**).

To an ice-cold solution of **3** (10 mmoles) in 2:1 tetrahydrofuran-methanol (25 mL), *N*-bromosuccinimide (12 mmoles) was added in portions. After 20 minutes, water (1 mL) was added and mixture was stirred for 3-4 hours. The contents were poured onto crushed ice. The separated solid was collected by filtration, dried and recrystallised from alcohol-benzene mixture.

General Procedure.

Semicarbazones of **2** and **4** (**5**).

A mixture of **2** or **4** (10 mmoles), semicarbazide hydrochloride (12 mmoles) and sodium acetate (15 mmoles) in ethanol (20 mL) was refluxed while stirring for 2-3 hours. The contents were cooled and poured onto ice-cold water. The separated solid was collected by filtration, washed, dried and recrystallised from alcohol.

General Procedure.

Phenyl Hydrazones of **2** and **4** (**6**).

To a solution of **2** or **4** (5 mmoles) in ethanol (15 mL), phenylhydrazine hydrochloride (7 mmoles) and sodium acetate (0.5 g) was added. The mixture was refluxed for 1-2 hours, concentrated and cooled. The separated solid was collected by filtration, washed, dried and recrystallised from methanol.

General Procedure.

5,7-Dimethyl-4-aryl-6-phenyl-4,5,6,7-tetrahydro-3-selena-1,2,5-triazaindene (**7**) and 7-Methyl-4-aryl-6-phenyl-6,7-dihydro-4*H*-5-thia-3-selena-1,2-diazaindene-5-oxide (**8**).

The semicarbazone **5** (5 mmoles) was dissolved in glacial acetic acid (15 mL) and warmed gently with stirring. To this, selenium dioxide (5 mmoles) was added portion wise during a period of 30 minutes at 60-70 °C and the stirring was continued for 4-5 hours. The reaction mixture was cooled and filtered onto crushed ice. The separated solid was collected by filtration,

washed with cold water, sodium bicarbonate solution and dried. The residue was purified through column chromatography (Silica gel; ethyl acetate-hexane, 1:3).

General Procedure.

5,7-Dimethyl-4-aryl-6-phenyl-4,5,6,7-tetrahydro-3-thia-1,2,5-triazaindene (**9**) and 7-Methyl-4-aryl-6-phenyl-6,7-dihydro-4H-3,5-dithia-1,2-diazaindene-5-oxide (**10**).

To a well cooled solution of semicarbazone **5** (5 mmoles) in dichloromethane (20 mL), an excess of thionyl chloride (3 mL) was added in portions while stirring and the mixture was allowed to attain room temperature. After stirring for 2-3 hours, the excess reagent was decomposed with cold saturated sodium carbonate solution. The organic layer was separated, washed with water and dried (anhydrous sodium sulfate). Evaporation of the solvent *in vacuo* resulted a residue, which was subjected to column chromatography (silica gel) with ethyl acetate-hexane (1:2) as eluents.

General Procedure.

5,7-Dimethyl-4-aryl-2,6-diphenyl-4,5,6,7-tetrahydro-2H-1,2,5-triaza-3-phosphaindene (**11**) and 7-Methyl-4-aryl-2,6-diphenyl-2,4,6,7-tetrahydro-5-thia-2H-1,2-diaza-3-phosphaindene-5-oxide (**12**).

To a stirred solution of phosphorous trichloride (15 mmoles) and dry diethyl ether (20 mL) under nitrogen atmosphere maintained at -5 to -10 °C, phenyl hydrazone **6** (5 mmoles) in dry ether (10 mL) was added drop wise. To this, triethylamine (20 mmoles) was added and stirring was continued for 3-4 hours. The ethereal layer was separated, washed with sodium bicarbonate solution, water and dried (anhydrous sodium sulfate). The ether was removed under reduced pressure and the resultant residue was purified by filtration through a column of silica gel using ethyl acetate-hexane (1:2) as eluent to furnish **11** or **12**.

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* Author to whom correspondence should be sent; e-mail: vkpuram2001@yahoo.com

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