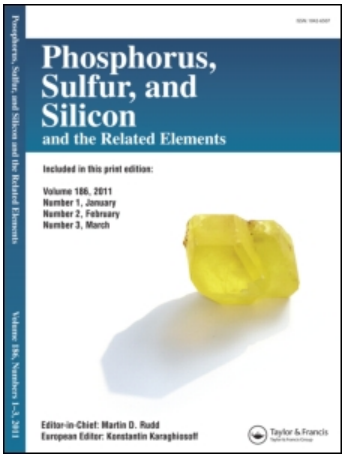


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# Cyclohexanones--Source for Selena/Thiadiazoles and Diazaphospholes

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# CYCLOHEXANONES—SOURCE FOR SELENA/THIADIAZOLES AND DIAZAPHOSPHOLES

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*Some new heterocyclic compounds containing selenadiazole, thiadiazole and diazaphosphole fused to cyclohexanones have been prepared and characterized by spectral data.*

*Keywords:* 1,1,2,3,6-pentasubstituted cyclohexan-4-ones; $\alpha$-keto-methylene group; 1,2,3-selenadiazoles; 1,2,3-thiadiazoles; 2H-1,2,3-diazaphospholes

## INTRODUCTION

Molecules with heteroaromatic rings are predominantly distributed in nature apart from their synthetic viability as valuable compounds. Incorporation of heteroatom within the framework of donor system is an important aspect in the designing of some such new synthetic molecules. In this perspective, a number of carbocyclic and heterocyclic systems with Michael acceptors, 1,5-diaryl-1,4-pentadien-3-ones, as synthons have been developed during the last one and half decades by our group. In fact, the double Michael addition of the latter have become a source for a variety of heterocyclic systems.[1–5] In the recent past, we were interested in the annelated heterocyclics, particularly 1,2,3-selena/thiadiazole rings fused to carbocyclic and heterocyclic rings systems.[6–16] In continuation of our study, we examined

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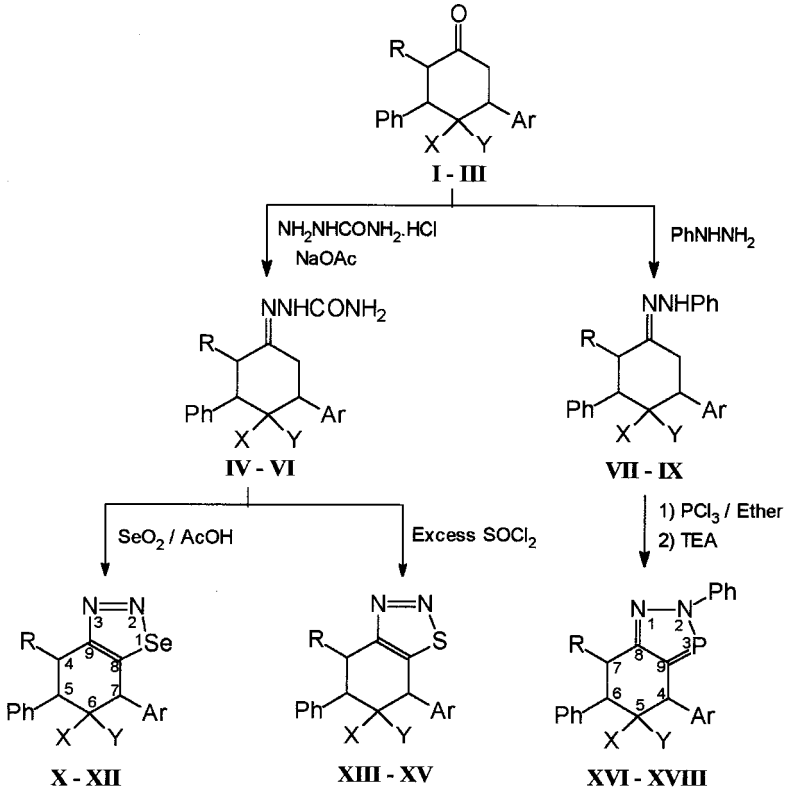
the reaction of 3-alkyl-2-phenyl-6-aryl-1,1-disubstituted cyclohexan-4-ones to obtain their fused 1,2,3-selena/thiadiazoles and 2H-1,2,3-diazaphospholes hitherto unreported in the literature.

## RESULTS AND DISCUSSION

The key intermediates 3-alkyl-2-phenyl-6-aryl-1,1-disubstituted cyclohexan-4-ones(**I–III**) were prepared from 2-alkyl-1-phenyl-5-aryl-1,4-pentadien-3-ones by double Michael addition of dimethyl malonate, ethyl cyanoacetate and dicyanomethane.[17] The $\alpha$-ketomethylene functionality in **I–III** has been made use for the development of fused 1,2,3-selena/thiadiazoles and 2H-1,2,3-diazaphosphole rings. The 4-alkyl-5-phenyl-7-aryl-6,6-dimethoxycarbonyl/6-cyano-6-ethoxycarbonyl/6,6-dicyano,-4,5,7-trihydrobenzo[*d*][1,2,3]-selenadiazoles (**X–XII**) were obtained by oxidative cyclization of the semicarbazones of **I–III** with selenium dioxide in acetic acid at 70°C.[18] However, Hurd-Mori reaction process[19] with excess thionyl chloride in dichloromethane at 0°C gave 4-alkyl-5-phenyl-7-aryl-6,6-dimethoxycarbonyl/6-cyano-6-ethoxycarbonyl/6,6-dicyano-4,5,7-trihydrobenzo[*d*][1,2,3]-thiadiazoles (**XIII–XV**). On the other hand, the 7-alkyl-2,6-diphenyl-4-aryl-5,5-dimethoxycarbonyl/5-cyano-5-ethoxycarbonyl/5,5-dicyano-4,6,7-trihydrobenzo[*d*]-2H-[1,2,3]-diazaphospholes (**XVI–XVIII**) have been prepared by cyclization of the phenyl hydrazones of **I–III** with phosphorous trichloride and triethylamine in ether at $-5$ to $-10$°C[20] (Scheme I). The physical data of these compounds are presented in the Table I.

The IR spectra ($\nu$, $cm^{-1}$) of **IV–VI** exhibited bands in the regions 1720–1765 (CO of ester), 2235–2260 (CN), 3200–3450 (NHCO and $CONH_2$), 1680–1700 and 1560–1580 ($CONH_2$), and 1650–1665 (C=N). The absence of bands due to semicarbazone and the presence of bands in the region 1430–1450 (N=N) and 750–690 (C-Se/S) supports the formation of selena/thiadiazoles (**X–XV**). Moreover, the bands at 3330–3360 (NH) and 1600–1620 (C=N), in addition to ester and cyano group absorption, were displayed by the phenylhydrazones, **VII–IX**. The absence of NH band and the presence of bands at 1585–1615 (C=N) and 980–1010 (P–N) confirms the formation of diazaphospholes (**XVI–XVIII**).

The $^1$H NMR spectra ($\delta$, ppm) of **IV–IX** may be rationalized by assuming that the two aryl groups might occupy more stable equatorial positions of the preferred chair conformation of the cyclohexane ring (see Figure 1). The methylene (H-5) and methine (H-6) protons of cyclohexane moiety are expected to exhibit an ABX splitting pattern. As a result, H-5 and H-6 might appear as doublet of doublet. However, amongst the



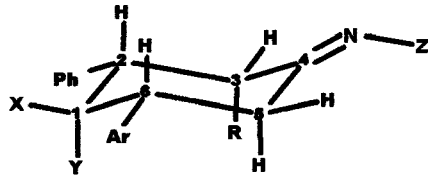

X, XIII, XVI : X = Y = $CO_2Me$

XI, XIV, XVII : X = CN, Y = $CO_2Et$

XII, XV, XVIII : X = Y = CN

| Compd | R | Ar |
|---|---|---|
| a | Me | Ph |
| b | Me | 4-MePh |
| c | Me | 4-OMePh |
| d | Et | Ph |
| e | Et | 4-ClPh |

**SCHEME 1**



**Z = NHCONH$_2$ (or) NHPh**

**FIGURE 1** Preferred conformation for IV–IX.

**TABLE I** Physical and Analytical Data of Compounds **X–XVIII**

| Compd. no. | Yield (%) | m.p. (°C) | Mol. formula (mol. wt.) | Found (calcd.) (%) | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| **$X_a$** | 68 | 134–136 | $C_{23}H_{22}N_2O_4Se$ (469.39) | 59.04 (58.85) | 4.81 (4.72) | 6.10 (5.97) |
| **$X_b$** | 64 | 125–127 | — | — | — | — |
| **$X_c$** | 66 | 140–142 | — | — | — | — |
| **$X_d$** | 60 | 121–123 | $C_{24}H_{24}N_2O_4Se$ (483.42) | 59.95 (59.63) | 5.14 (5.00) | 5.56 (5.79) |
| **$X_e$** | 64 | 138–140 | — | — | — | — |
| **$XI_a$** | 65 | 144–146 | $C_{23}H_{21}N_3O_2Se$ (450.39) | 61.20 (61.33) | 4.75 (4.70) | 9.18 (9.33) |
| **$XI_b$** | 63 | 118–120 | — | — | — | — |
| **$XI_c$** | 65 | 136–138 | — | — | — | — |
| **$XI_d$** | 62 | 128–130 | $C_{24}H_{23}N_3O_2Se$ (464.42) | 61.77 (62.07) | 5.14 (4.99) | 8.86 (9.05) |
| **$XI_e$** | 66 | 142–144 | — | — | — | — |
| **$XII_a$** | 58 | 126–128 | $C_{21}H_{16}N_4Se$ (403.34) | 62.30 (62.53) | 4.18 (4.00) | 13.65 (13.89) |
| **$XII_b$** | 55 | 144–146 | — | — | — | — |
| **$XII_c$** | 60 | 131–133 | — | — | — | — |
| **$XII_d$** | 57 | 120–122 | $C_{22}H_{18}N_4Se$ (417.37) | 63.73 (63.31) | 4.55 (4.35) | 13.68 (13.42) |
| **$XII_e$** | 62 | 136–138 | — | — | — | — |
| **$XIII_a$** | 65 | 147–149 | $C_{23}H_{22}N_2O_4S$ (422.50) | 65.21 (65.38) | 5.38 (5.25) | 6.44 (6.63) |
| **$XIII_b$** | 60 | 120–122 | — | — | — | — |
| **$XIII_c$** | 58 | 141–143 | — | — | — | — |
| **$XIII_d$** | 60 | 134–136 | $C_{24}H_{24}N_2O_4S$ (436.52) | 65.81 (66.03) | 5.76 (5.54) | 6.20 (6.42) |
| **$XIII_e$** | 56 | 152–154 | — | — | — | — |
| **$XIV_a$** | 65 | 140–142 | $C_{23}H_{21}N_3O_2S$ (403.50) | 68.24 (68.46) | 5.41 (5.25) | 10.22 (10.41) |
| **$XIV_b$** | 57 | 118–120 | — | — | — | — |
| **$XIV_c$** | 62 | 144–146 | — | — | — | — |
| **$XIV_d$** | 58 | 122–124 | $C_{24}H_{23}N_3O_2S$ (417.52) | 69.28 (69.04) | 5.35 (5.55) | 10.15 (10.06) |
| **$XIV_e$** | 60 | 136–138 | — | — | — | — |
| **$XV_a$** | 55 | 135–137 | $C_{21}H_{16}N_4S$ (356.45) | 70.52 (70.76) | 4.73 (4.52) | 15.94 (15.72) |
| **$XV_b$** | 58 | 119–121 | — | — | — | — |
| **$XV_c$** | 62 | 140–142 | — | — | — | — |
| **$XV_d$** | 57 | 128–130 | $C_{22}H_{18}N_4S$ (370.47) | 71.51 (71.32) | 4.76 (4.90) | 14.93 (15.12) |
| **$XV_e$** | 55 | 145–147 | — | — | — | — |
| **$XVI_a$** | 70 | 160–162 | $C_{29}H_{27}N_2O_4P$ (498.51) | 69.58 (69.87) | 5.33 (5.46) | 5.81 (5.62) |

**TABLE I** Physical and Analytical Data of Compounds **X–XVIII** *(Continued)*

| Compd. no. | Yield (%) | m.p. (°C) | Mol. formula (mol. wt.) | Found (calcd.) (%) | | |
|---|---|---|---|---|---|---|
| | | | | C | H | N |
| **XVI$_b$** | 65 | 144–146 | — | — | — | — |
| **XVI$_c$** | 70 | 173–175 | — | — | — | — |
| **XVI$_d$** | 65 | 158–160 | $C_{30}H_{29}N_2O_4P$ (512.54) | 70.04 (70.30) | 5.42 (5.70) | 5.26 (5.47) |
| **XVI$_e$** | 63 | 155–157 | — | — | — | — |
| **XVII$_a$** | 65 | 171–173 | $C_{29}H_{26}N_3O_2P$ (479.51) | 72.44 (72.64) | 5.29 (5.47) | 8.98 (8.76) |
| **XVII$_b$** | 60 | 150–152 | — | — | — | — |
| **XVII$_c$** | 62 | 156–158 | — | — | — | — |
| **XVII$_d$** | 64 | 141–143 | $C_{30}H_{28}N_3O_2P$ (493.54) | 72.83 (73.01) | 5.50 (5.72) | 8.78 (8.51) |
| **XVII$_e$** | 60 | 175–177 | — | — | — | — |
| **XVIII$_a$** | 65 | 168–170 | $C_{27}H_{21}N_4P$ (432.46) | 74.73 (74.99) | 4.70 (4.89) | 13.20 (12.96) |
| **XVIII$_b$** | 63 | 150–152 | — | — | — | — |
| **XVIII$_c$** | 66 | 162–164 | — | — | — | — |
| **XVIII$_d$** | 60 | 156–158 | $C_{28}H_{23}N_4P$ (446.48) | 75.07 (75.32) | 5.43 (5.19) | 12.81 (12.55) |
| **XVIII$_e$** | 64 | 145–147 | — | — | — | — |



other methine protons (H-2 & H-3), the H-2 should display a doublet, while H-3 a multiplet. Infact, the spectra ($\delta$, ppm) displayed such a type of splitting pattern (see Table II). The two doublet of doublets observed in the spectra around 2.60 and 4.20 were assigned to $H_e$-5 and $H_a$-6 respectively. The coupling constants ($J$) for them were found to be around 13.7 and 4.2 Hz. On the other hand, the doublet around 3.85 observed was attributed to $H_a$-2, whose coupling constant was 6.4 Hz. The multiplet exhibited around 2.50 was assigned to $H_a$-3. Furthermore, two signals observed around 10.32–10.44 (NHCO) and 7.20–7.35 ($CONH_2$) for the semicarbazone moiety and a signal around 8.23–8.30 (NH) for the phenylhydrazone moiety, which were disappeared on deuteration. The carbomethoxy groups appeared as singlets at two distinct regions (3.35 and 3.55), while for carboethoxy groups as multiplet around 3.75. The coupling constants of $H_a$-2 and H-3 and $H_a$-6 and H-5 were in agreement with those of *syn* axial-eqatorial H, H coupling. This suggests that the substituents at $C_2$ and $C_6$ positions are favorably disposed to *cis*-1,3 diequatorial orientation, while the substituent at $C_3$ with respect to $C_2$ also possess cis orientation. Thus all the three substituents are disposed to *cis* orientation only with respect to each other.

**TABLE II** NMR Spectral Data of Compounds **IV–IX** and **X–XVIII**

| Compd. no. | $^1$H NMR ($\delta$, ppm) | $^{13}$C NMR ($\delta$, ppm) |
|---|---|---|
| **IV$_a$** | 0.97 (d, 3H, $CH_3$), 2.50 (dd, 1H, $H_e$-5, $J$ = 13.7 & 4.2 Hz), 2.98 (t, 1H, $H_a$-5), 3.35 & 3.55 (s, 6H, 2-$OCH_3$), 3.88 (d, 1H, H-2, $J$ = 6.4 Hz), 4.03 (q, 1H, H-3), 4.21 (dd, 1H, H-6, $J$ = 13.4 & 4.0 Hz), 7.03–7.56 (m, 12H, Ar—H & $CONH_2$), 10.43 (s, 1H, NHCO) | 12.90 ($CH_3$), 41.58 ($C_5$), 44.15 ($C_6$) 46.16 ($C_3$), 50.13 ($C_2$), 51.50 & 51.82 (2-$OCH_3$), 63.30 ($C_1$), 154.28 ($C_4$), 159.36 ($CONH_2$), 167.73 & 170.04 (2-$\underline{C}OOCH_3$) |
| **V$_a$** | 0.94–1.05 (m, 6H, $CH_3$ & $OCH_2C\underline{H}_3$), 2.62 (dd, 1H, $H_e$-5, $J$ = 13.6 & 4.2 Hz), 3.05 (t, 1H, $H_a$-5), 3.30–3.38 (m, 1H, H-3), 3.70–3.95 (m, 4H, H-2, $OC\underline{H}_2CH_3$ & H-6), 7.18–7.72 (m, 12H, Ar—H & $CONH_2$), 10.32 (s, 1H, NHCO) | 11.32 ($OCH_2C\underline{H}_3$), 13.05 ($CH_3$) 41.97 ($C_6$), 42.82 ($C_5$), 46.01 ($C_3$), 51.78 ($C_2$), 56.10 ($C_1$), 62.46 ($O\underline{C}H_2CH_3$), 116.83 (CN), 154.64 ($C_4$), 158.05 ($CONH_2$), 165.22 ($\underline{C}OOC_2H_5$) |
| **VI$_a$** | 0.88 (d, 3H, $CH_3$), 2.74 (dd, 1H, $H_e$-5, $J$ = 13.4 & 4.1 Hz), 3.10 (t, 1H, $H_a$-5), 3.23 (q, 1H, H-3), 3.67 (dd, 1H, H-6, $J$ = 13.6 & 4.1 Hz), 3.92 (d, H-2, $J$ = 6.3 Hz) 7.08–7.52 (m, 12H, Ar—H & $CONH_2$), 10.39 (s, 1H, NHCO) | 12.16 ($CH_3$), 41.03 ($C_5$), 43.75 ($C_6$), 44.31 ($C_3$), 46.58 ($C_1$), 51.05 ($C_2$), 112.84 & 114.13 (2 CN), 154.32 ($C_4$), 159.82 ($CONH_2$) |
| **VII$_a$** | 1.05 (d, 3H, $CH_3$), 2.54 (dd, 1H, $H_e$-5, $J$ = 13.8 & 4.2 Hz), 3.02 (t, 1H, $H_a$-5), 3.42 & 3.60 (s, 6H, 2-$OCH_3$), 3.85 (d, 1H, H-2, $J$ = 6.5 Hz), 4.12–4.24 (m, 2H, H-3 & H-6), 7.09–7.62 (m, 15H, Ar—H), 8.23 (s, 1H, NH) | 13.13 ($CH_3$), 40.95 ($C_5$), 43.88 ($C_6$), 46.36 ($C_3$), 49.93 ($C_2$), 51.32 & 52.54 (2-$OCH_3$), 63.02 ($C_1$), 150.08 ($C_4$), 168.75 & 170.26 (2-$\underline{C}OOCH_3$) |
| **VIII$_a$** | 0.92–1.10 (m, 6H, $CH_3$ & $OCH_2C\underline{H}_3$), 2.60 (dd, 1H, $H_e$-5, $J$ = 13.7 & 4.2 Hz), 3.08 (t, 1H, $H_a$-5), 3.35–3.42 (m, 1H, H-3), 3.62–3.68 (m, 2H, $OC\underline{H}_2CH_3$), 3.79 (d, 1H, H-2, $J$ = 6.6 Hz), 3.90–4.02 (m, 1H, H-6), 7.09–7.52 (m, 15H, Ar—H), 8.30 (s, 1H, NH) | 11.66 ($OCH_2C\underline{H}_3$), 13.22 ($CH_3$) 42.23 ($C_6$), 43.97 ($C_5$), 45.86 ($C_3$), 51.52 ($C_2$), 56.31 ($C_1$), 62.15 ($O\underline{C}H_2CH_3$), 116.34 (CN), 151.16 ($C_4$), 165.73 ($\underline{C}OOC_2H_5$) |
| **IX$_a$** | 0.97 (d, 3H, $CH_3$), 2.70 (dd, 1H, $H_e$-5, $J$ = 13.6 & 4.0 Hz), 3.13 (t, 1H, $H_a$-5), 3.22–3.28 (m, 1H, H-3), 3.60 (dd, 1H, H-6, $J$ = 13.7 & 4.1 Hz), 3.96 (d, H-2, $J$ = 6.4 Hz) 7.05–7.55 (m, 15H, Ar—H), 8.28 (s, 1H, NH) | 12.73 ($CH_3$), 41.22 ($C_5$), 43.93 ($C_6$), 44.94 ($C_3$), 46.87 ($C_1$), 50.44 ($C_2$), 112.36 & 114.00 (2 CN), 150.82 ($C_4$) |
| **X$_a$** | 0.92 (d, 3H, $CH_3$), 2.98–3.07 (m, 1H, H-4), 3.31 & 3.56 (s, 6H, 2-$OCH_3$), 3.66 (d, 1H, H-5, $J$ = 6.8 Hz), 4.83 (s, 1H, H-7), 7.05–7.52 (m, 10H, Ar—H) | 14.83 ($CH_3$), 44.22 ($C_4$), 46.14 ($C_7$), 49.78 ($C_5$), 51.42 & 52.08 (2-$OCH_3$), 63.32 ($C_6$), 144.27 ($C_8$), 151.45 ($C_9$), 167.95 & 169.63 (2-$\underline{C}OOCH_3$) |

**TABLE II** NMR Spectral Data of Compounds **IV–IX** and **X–XVIII** *(Continued)*

| Compd. no. | $^1$H NMR ($\delta$, ppm) | $^{13}$C NMR ($\delta$, ppm) |
|---|---|---|
| **$X_b$** | 0.89 (d, 3H, $CH_3$), 2.23 (s, 3H, Ar—$CH_3$), 3.05–3.16 (m, 1H, H-4), 3.30 & 3.58 (s, 6H, 2-$OCH_3$), 3.72 (d, 1H, H-5, $J$ = 6.6 Hz), 4.92 (s, 1H, H-7), 7.08–7.64 (m, 9H, Ar—H) | — |
| **$X_d$** | 0.78 (t, 3H, $CH_2C\underline{H}_3$), 1.35 (q, 1H, $C\underline{H}_2CH_3$), 1.58–1.66 (m, 1H, $C\underline{H}_2CH_3$), 3.06 (q, 1H, H-4), 3.25 & 3.54 (s, 6H, 2-$OCH_3$), 3.70 (d, 1H, H-5, $J$ = 6.9 Hz), 5.01 (s, 1H, H-7), 7.12–7.59 (m, 10H, Ar—H) | 11.76 ($CH_2\underline{C}H_3$), 20.18 ($\underline{C}H_2CH_3$), 45.18 ($C_4$), 46.23 ($C_7$), 49.54 ($C_5$), 51.35 & 52.12 (2-$OCH_3$), 63.85 ($C_6$), 143.72 ($C_8$), 152.58 ($C_9$), 168.24 & 171.05 (2-$\underline{C}OOCH_3$) |
| **$XI_a$** | 0.90–1.03 (m, 6H, $CH_3$ & $OCH_2C\underline{H}_3$), 3.02–3.10 (m, 1H, H-4), 3.73 (d, 1H, H-5, $J$ = 6.7 (Hz), 3.84–3.92 (m, 2H, $OC\underline{H}_2CH_3$), 4.96 (s, 1H, H-7), 7.14–7.72 (m, 10H, Ar—H) | 11.88 ($OCH_2\underline{C}H_3$), 13.70 ($CH_3$) 44.84 ($C_4$), 46.55 ($C_7$), 48.02 ($C_5$), 56.75 ($C_6$), 62.13 ($O\underline{C}H_2CH_3$), 113.82 (CN), 145.16 ($C_8$), 151.27 ($C_9$), 165.25 ($\underline{C}OOC_2H_5$) |
| **$XI_c$** | 0.94–1.12 (m, 6H, $CH_3$ & $OCH_2C\underline{H}_3$), 2.95–3.04 (m, 1H, H-4), 3.68 (d, 1H, H-5, $J$ = 6.8 Hz), 3.79 (s, 3H, Ar—$OCH_3$), 3.86–3.93 (m, 2H, $OC\underline{H}_2CH_3$), 5.04 (s, 1H, H-7), 7.00–7.81 (m, 9H, Ar—H) | — |
| **$XI_d$** | 0.84 (t, 3H, $CH_2C\underline{H}_3$), 1.06 (t, 3H, $OCH_2C\underline{H}_3$), 1.43–1.55 (m, 2H, $CH_2CH_3$), 3.15 (q, 1H, H-4), 3.64 (d, 1H, H-5, $J$ = 6.7 Hz), 3.83–3.95 (m, 2H, $OC\underline{H}_2CH_3$), 4.99 (s, 1H, H-7), 7.03–7.70 (m, 10H, Ar—H) | 11.09 ($CH_2\underline{C}H_3$), 12.86 ($OCH_2\underline{C}H_3$), 21.03 ($\underline{C}H_2CH_3$), 45.38 ($C_4$), 46.34 ($C_7$), 48.25 ($C_5$), 57.02 ($C_6$), 62.50 ($O\underline{C}H_2CH_3$), 113.21 (CN), 144.63 ($C_8$), 151.54 ($C_9$), 164.90 ($\underline{C}OOC_2H_5$) |
| **$XII_a$** | 0.95 (d, 3H, $CH_3$), 3.07–3.18 (m, 1H, H-4), 3.78 (d, 1H, H-5, $J$ = 6.9 Hz), 4.94 (s, 1H, H-7), 7.08–7.68 (m, 10H, Ar—H) | 13.05 ($CH_3$), 44.67 ($C_4$), 45.94 ($C_7$), 47.18 ($C_6$), 48.93 ($C_5$), 114.63 & 116.45 (2-CN), 146.28 ($C_8$), 152.33 ($C_9$) |
| **$XII_d$** | 0.88 (t, 3H, $CH_2C\underline{H}_3$), 1.43 (q, 1H, $C\underline{H}_2CH_3$), 1.59–1.70 (m, 1H, $C\underline{H}_2CH_3$), 3.08–3.20 (m, 1H, H-4), 3.67 (d, 1H, H-5, $J$ = 6.8 Hz), 5.05 (s, 1H, H-7), 7.11–7.80 (m, 10H, Ar—H) | 11.83 ($CH_2\underline{C}H_3$), 20.32 ($\underline{C}H_2CH_3$), 44.42 ($C_4$), 46.24 ($C_7$), 47.26 ($C_6$), 48.77 ($C_5$), 114.32 & 116.53 (2-CN), 145.15 ($C_8$), 151.81 ($C_9$) |
| **$XIII_a$** | 0.96 (d, 3H, $CH_3$), 3.03–3.18 (m, 1H, H-4), 3.35 & 3.54 (s, 6H, 2-$OCH_3$), 3.65 (d, 1H, H-5, $J$ = 6.7 Hz), 4.91 (s, 1H, H-7), 7.07–7.60 (m, 10H, Ar—H) | 14.31 ($CH_3$), 44.73 ($C_4$), 46.42 ($C_7$), 50.04 ($C_5$), 51.74 & 52.06 (2-$OCH_3$), 63.27 ($C_6$), 138.64 ($C_8$), 150.83 ($C_9$), 168.22 & 170.05 (2-$\underline{C}OOCH_3$) |

*(Continued on next page)*

**TABLE II** NMR Spectral Data of Compounds **IV–IX** and **X–XVIII** *(Continued)*

| Compd. no. | $^1$H NMR ($\delta$, ppm) | $^{13}$C NMR ($\delta$, ppm) |
|---|---|---|
| **XIII$_c$** | 1.02 (d, 3H, $CH_3$), 3.00–3.13 (m, 1H, H-4), 3.28 & 3.51 (s, 6H, 2-$OCH_3$), 3.71 (d, 1H, H-5, $J$ = 6.9 Hz), 3.80 (s, 3H, Ar—$OCH_3$), 5.03 (s, 1H, H-7), 7.05–7.65 (m, 9H, Ar—H) | — |
| **XIII$_d$** | 0.81 (t, 3H, $CH_2C\underline{H}_3$), 1.33 (q, 1H, $C\underline{H}_2CH_3$), 1.54–1.68 (m, 1H, $C\underline{H}_2CH_3$), 2.96–3.05 (m, 1H, H-4), 3.23 & 3.55 (s, 6H, 2-$OCH_3$), 3.74 (d, 1H, H-5, $J$ = 6.8 Hz), 5.10 (s, 1H, H-7), 7.09–7.64 (m, 10H, Ar—H) | 11.85 ($CH_2\underline{C}H_3$), 20.73 ($\underline{C}H_2CH_3$), 44.95 ($C_4$), 46.17 ($C_7$), 50.17 ($C_5$), 51.28 & 52.72 (2-$OCH_3$), 63.12 ($C_6$), 139.03 ($C_8$), 151.52 ($C_9$), 168.86 & 169.92 (2-$\underline{C}OOCH_3$) |
| **XIV$_a$** | 0.92–1.06 (m, 6H, $CH_3$ & $OCH_2C\underline{H}_3$), 3.08–3.18 (m, 1H, H-4), 3.78 (d, 1H, H-5, $J$ = 6.9 Hz), 3.82–3.91 (m, 2H, $OC\underline{H}_2CH_3$), 5.00 (s, 1H, H-7), 7.15–7.70 (m, 10H, Ar—H) | 12.37 ($OCH_2\underline{C}H_3$) 14.06 ($CH_3$), 45.13 ($C_4$), 46.78 ($C_7$), 48.23 ($C_5$), 56.54 ($C_6$), 63.05 ($O\underline{C}H_2CH_3$), 113.15 (CN), 140.34 ($C_8$), 150.76 ($C_9$), 164.88 ($\underline{C}OOC_2H_5$) |
| **XIV$_b$** | 0.87 (d, 3H, $CH_3$), 0.96–1.10 (m, 3H, $OCH_2C\underline{H}_3$), 2.20 (s, 3H, Ar—$CH_3$), 3.11–3.23 (m, 1H, H-4), 3.74 (d, 1H, H-5, $J$ = 6.7 Hz), 3.85–3.95 (m, 2H, $OC\underline{H}_2CH_3$), 4.96 (s, 1H, H-7), 7.05–7.70 (m, 9H, Ar—H) | — |
| **XIV$_d$** | 0.79 (t, 3H, $CH_2C\underline{H}_3$), 0.93–1.04 (m, 3H, $OCH_2C\underline{H}_3$), 1.38–1.51 (m, 2H, $C\underline{H}_2CH_3$), 3.22 (q, 1H, H-4), 3.68 (d, 1H, H-5, $J$ = 6.8 Hz), 3.81–3.93 (m, 2H, $OC\underline{H}_2CH_3$), 5.05 (s, 1H, H-7), 7.08–7.67 (m, 10H, Ar—H) | 11.35 ($CH_2\underline{C}H_3$), 13.07 ($OCH_2\underline{C}H_3$), 20.84 ($\underline{C}H_2CH_3$), 45.61 ($C_4$), 47.04 ($C_7$), 48.58 ($C_5$), 56.47 ($C_6$), 62.83 ($O\underline{C}H_2CH_3$), 112.96 (CN), 138.85 ($C_8$), 150.32 ($C_9$), 165.06 ($\underline{C}OOC_2H_5$) |
| **XV$_a$** | 0.98 (d, 3H, $CH_3$), 3.04–3.13 (m, 1H, H-4), 3.80 (d, 1H, H-5, $J$ = 6.8 Hz), 4.98 (s, 1H, H-7), 7.02–7.72 (m, 10H, Ar—H) | 13.80 ($CH_3$), 44.82 ($C_4$), 45.89 ($C_7$), 46.97 ($C_6$), 49.12 ($C_5$), 114.25 & 116.07 (2-CN), 140.35 ($C_8$), 151.23 ($C_9$) |
| **XV$_d$** | 0.84 (t, 3H, $CH_2C\underline{H}_3$), 1.36 (q, 1H, $C\underline{H}_2CH_3$), 1.60–1.70 (m, 1H, $C\underline{H}_2CH_3$), 3.14–3.22 (m, 1H, H-4), 3.72 (d, 1H, H-5, $J$ = 6.7 Hz), 5.01 (s, 1H, H-7), 7.05–7.70 (m, 10H, Ar—H) | 11.68 ($CH_2\underline{C}H_3$), 19.97 ($\underline{C}H_2CH_3$), 45.08 ($C_4$), 46.35 ($C_7$), 47.11 ($C_6$), 49.18 ($C_5$), 114.63 & 116.14 (2-CN), 137.94 ($C_8$), 150.84 ($C_9$) |
| **XVI$_a$** | 1.06 (d, 3H, $CH_3$), 3.12–3.22 (m, 1H, H-7), 3.32 & 3.47 (s, 6H, 2-$OCH_3$), 3.81 (d, 1H, H-6, $J$ = 6.9 Hz), 4.81 (s, 1H, H-4), 7.08–7.67 (m, 15H, Ar—H) | 13.88 ($CH_3$), 45.95 ($C_7$), 48.23 ($C_4$), 51.04 ($C_6$), 52.03 & 52.47 (2-$OCH_3$), 63.68 ($C_5$), 147.52 ($C_8$), 166.03 ($C_9$, $J_{CP}$ = 54.2 Hz), 169.15 & 170.22 (2-$COOCH_3$) |

**TABLE II** NMR Spectral Data of Compounds **IV–IX** and **X–XVIII** *(Continued)*

| Compd. no. | $^1$H NMR ($\delta$, ppm) | $^{13}$C NMR ($\delta$, ppm) |
|---|---|---|
| **XVI$_b$** | 1.02 (d, 3H, $CH_3$), 2.23 (s, 3H, Ar—$CH_3$), 3.15–3.23 (m, 1H, H-7), 3.38 & 3.50 (s, 6H, 2-$OCH_3$), 3.78 (d, 1H, H-6, $J$ = 6.8 Hz), 4.83 (s, 1H, H-4), 6.97–7.74 (m, 14H, Ar—H) | — |
| **XVI$_d$** | 0.86 (t, 3H, $CH_2C\underline{H}_3$), 1.28 (q, 1H, $C\underline{H}_2CH_3$), 1.55–1.67 (m, 1H, $C\underline{H}_2CH_3$), 3.20 (m, 1H, H-7), 3.28 & 3.45 (s, 6H, 2-$OCH_3$), 3.85 (d, 1H, H-6, $J$ = 6.8 Hz), 4.85 (s, 1H, H-4), 7.03–7.70 (m, 15H, Ar—H) | 11.43 ($CH_2\underline{C}H_3$), 20.82 ($\underline{C}H_2CH_3$), 46.26 ($C_7$), 48.57 ($C_4$), 51.29 ($C_6$), 52.15 & 52.69 (2-$OCH_3$), 64.04 ($C_5$), 148.18 ($C_8$), 165.64 ($C_9$, $J_{CP}$ = 53.3 Hz), 168.52 & 169.87 (2-$\underline{C}OOCH_3$) |
| **XVII$_a$** | 0.83 (t, 3H, $OCH_2C\underline{H}_3$) 1.16 (d, 3H, $CH_3$), 3.14–3.25 (m, 1H, H-7), 3.80 (d, 1H, H-6, $J$ = 6.7 Hz), 3.88–3.95 (m, 2H, $OC\underline{H}_2CH_3$), 4.91 (s, 1H, H-4), 7.02–7.68 (m, 15H, Ar—H) | 12.06 ($OCH_2\underline{C}H_3$) 14.22 ($CH_3$), 44.88 ($C_7$), 48.02 ($C_4$), 51.00 ($C_6$), 57.26 ($C_5$), 62.93 ($O\underline{C}H_2CH_3$), 114.31 (CN), 148.04 ($C_8$), 163.35 ($\underline{C}OOC_2H_5$), 167.78 ($C_9$, $J_{CP}$ = 52.1 Hz) |
| **XVII$_c$** | 0.88–1.13 (m, 6H, $CH_3$ & $OCH_2C\underline{H}_3$), 3.16–3.24 (m, 1H, H-7), 3.72 (s, 3H, Ar—$OCH_3$), 3.78 (d, 1H, H-6, $J$ = 6.8 Hz), 3.85–3.95 (m, 2H, $OC\underline{H}_2CH_3$), 4.87 (s, 1H, H-4), 6.98–7.76 (m, 14H, Ar—H) | — |
| **XVII$_d$** | 0.80 (t, 3H, $CH_2C\underline{H}_3$), 1.08 (t, 3H, $OCH_2C\underline{H}_3$), 1.32–1.48 (m, 2H, $C\underline{H}_2CH_3$), 3.18–3.30 (q, 1H, H-7), 3.76 (d, 1H, H-6, $J$ = 6.9 Hz), 3.83–3.94 (m, 2H, $OC\underline{H}_2CH_3$), 4.84 (s, 1H, H-4), 7.04–7.68 (m, 15H, Ar—H) | 10.98 ($CH_2\underline{C}H_3$), 12.22 ($OCH_2\underline{C}H_3$), 21.47 ($\underline{C}H_2CH_3$), 45.36 ($C_7$), 48.23 ($C_4$), 51.08 ($C_6$), 56.75 ($C_5$), 62.54 ($O\underline{C}H_2CH_3$), 113.28 (CN), 148.93 ($C_8$), 163.21 ($\underline{C}OOC_2H_5$), 166.83 ($C_9$, $J_{CP}$ = 54.8 Hz) |
| **XVIII$_a$** | 0.96 (d, 3H, $CH_3$), 3.15–3.24 (m, 1H, H-7), 3.87 (d, 1H, H-6, $J$ = 6.7 Hz), 4.80 (s, 1H, H-4), 7.03–7.70 (m, 15H, Ar—H) | 13.25 ($CH_3$), 45.38 ($C_7$), 46.82 ($C_4$), 47.46 ($C_5$), 52.14 ($C_6$), 113.96 & 115.37 (2-CN), 147.68 ($C_8$), 167.79 ($C_9$, $J_{CP}$ = 53.8 Hz) |
| **XVIII$_d$** | 0.82 (t, 3H, $CH_2C\underline{H}_3$), 1.26 (q, 1H, $C\underline{H}_2CH_3$), 1.54–1.68 (m, 1H, $C\underline{H}_2CH_3$), 3.21 (m, 1H, H-7), 3.80 (d, 1H, H-6, $J$ = 6.9 Hz), 4.90 (s, 1H, H-4), 6.98–7.70 (m, 15H, Ar—H) | 11.28 ($CH_2\underline{C}H_3$), 20.96 ($\underline{C}H_2CH_3$), 45.17 ($C_7$), 46.03 ($C_4$), 47.85 ($C_5$), 50.77 ($C_6$), 114.14 & 115.92 (2-CN), 148.26 ($C_8$), 165.79 ($C_9$, $J_{CP}$ = 52.2 Hz) |

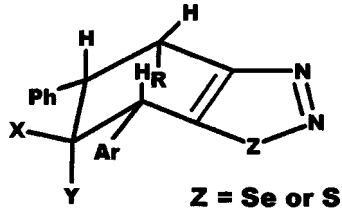



**FIGURE 2** Preferred conformation for X–XV.

Furthermore, the 1,2,3-selena/thiadiazoles and diazaphospholes could also be almost in the same plane as that of cyclohexene as per the Drieding model (see Figures 2 and 3). Thus it may be observed that selena/thiadiazole or diazaphosphole moiety is in the average plane of cyclohexene half chair conformation. This is truly reflected in the **2D** and **3D** computer simulated models also. The $^1$H NMR spectra of **X–XVIII** should give three different signals for methine protons of cyclohexene moiety. A multiplet in the region 2.95–3.23 (H-4 of **X–XV** and H-7 of **XVI–XVIII**), a doublet around 3.64–3.80 (H-5 of **X–XV** and H-6 of **XVI–XVIII**) and a singlet between 4.80–5.05 (H-7 of **X–XV** and H-4 of **XVI–XVIII**). However, the coupling constants for H-4 and H-5/H-7 and H-6 were observed around 6.70–6.90 Hz. The methine proton adjacent to double bond (H-7/H-4) appears at downfield region due to anisotropic effect.[12] The $\delta_H$ values observed for **X–XVIII** are given in Table II.

It is of interest to observe that many stereoisomers are possible in all the precursors and products since they possess 3 or 4 chiral centers, however, only one isomer was predominantly observed in every case as explained above. The $\delta_C$ values for these compounds derived from their $^{13}$C NMR spectra were also incorporated in Table II, which supports the structural assignments arrived on the basis of $^1$H NMR spectra. Thus, it is evident that the semicarbazones/phenylhydrazones and $\alpha$-methylene group of cyclic ketones are involved in the cyclization process.

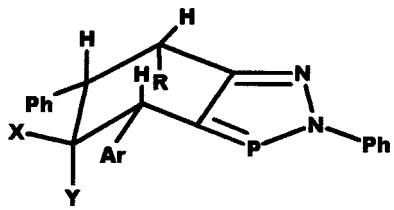



**FIGURE 3** Preferred conformation for XVI–XVIII.

## EXPERIMENTAL

Melting points were determined in open capillaries on Veego Scientific PMP-DM apparatus and are uncorrected. The purity of the compounds was checked by thin layer chromatography (Silica gel H, BDH; ethyl acetate: hexane, 1:3). The IR spectra were recorded on Perkin-Elmer 1600 series FT Infrared spectrometer in KBr pellets ($\nu$ in $cm^{-1}$). The $^1H$ NMR and $^{13}C$ NMR spectra were recorded in $CDCl_3$ on Brucker DPX 300 spectrometer with TMS as an internal standard ($\delta$ in ppm). The microanalytical data were obtained from Vikram Sarabhai Space Centre, Trivandrum, India.

### General Procedure for the Preparation of Semicarbazones (IV–VI)

A mixture of semicarbazide hydrochloride (10 mmol) and sodium acetate trihydrate (20 mmol) was dissolved in methanol (20 ml) and the residue (NaCl) was filtered off. The compounds **I–III** (10 mmol) in methanol was added to the filtrate and the contents were heated on water bath for 3–5 h. The reaction mixture was concentrated, cooled and poured onto crushed ice. The solid obtained was filtered, dried, and recrystallized from ethanol to obtain pure **IV–VI**.



### General Procedure for the Preparation of Selenadiazoles (X–XII)

The semicarbazones, **IV–VI** (3 mmol) were dissolved in glacial acetic acid (20 ml) and warmed gently with stirring until a clear solution was obtained. Selenium dioxide (3 mmol) in portions was then added during a period of 0.5 h with stirring. The contents were stirred at 60–70°C until the evolution of gas ceased and the deposited selenium was removed by filtration. The filtrate was poured onto crushed ice and the collected solid was washed with cold water and sodium bicarbonate solution. The compound thus obtained was purified on a column of silica gel (60–120 mesh, BDH) using hexane: ethyl acetate (1:1) as eluent.

### General Procedure for the Preparation of Thiadiazoles (XIII–XV)

Each compound, **IV–VI** (3 mmol) was added to an excess of thionyl chloride (5 ml) at 0°C in a portionwise manner with stirring and allowed to attain room temperature. Then dichloromethane (20 ml) was added and resulting mixture was decomposed with cold saturated sodium

carbonate solution. The organic layer was separated, washed thoroughly with water, and then dried over anhydrous sodium sulfate. The solvent was evaporated under vacuo. The crude product obtained was purified by column chromatography using silica gel (60–120 mesh, BDH) with hexane: ethyl acetate (1:1) as eluent.

## General Procedure for the Preparation of Phenylhydrazones (VII–IX)

To the compounds **I–III** (5 mmol) dissolved in methanol (25 ml), phenylhydrazine (5 mmol) was added and refluxed for 2–3 h. The reaction mixture was concentrated to 10–15 ml and then cooled. The solid separated was filtered, washed with water, dried and recrystallised from alcohol.

## General Procedure for the Preparation of Diazaphospholes (XVI–XVIII)

Phosphorous trichloride (10 mmol) was added to dry ether at −5 to −10°C under nitrogen atmosphere with stirring. To this, phenylhydrazones, **VII–IX** (3 mmol) dissolved in dry ether, was added slowly dropwise and then triethylamine (12 mmol) was added. Stirring was continued for 2–3 h and the contents were brought to laboratory temperature. Evaporation of the ethereal layer under reduced pressure gave a solid product, which was purified by filtration through a column of silica gel (60–120 mesh, BDH) with hexane: ethyl acetate (1.5:1) as eluent.



## REFERENCES

[1] D. Bhaskar Reddy, V. Padmavathi, and S. Reddy, *Sulfur Letters*, **13**(3), 123 (1991).
[2] D. Bhaskar Reddy, V. Padmavathi, and M. Muralidhar Reddy, *Indian J. Chem*., **31B,** 407 (1992).
[3] D. Bhaskar Reddy, V. Padmavathi, and P. V. Ramana Reddy, *Indian J. Chem*., **31B,** 774 (1992).
[4] D. Bhaskar Reddy, V. Padmavathi, B. Seenaiah, and A. Padmaja, *Heteroatom Chem*., **4**(1), 55 (1993).
[5] D. Bhaskar Reddy, N. Chendrasekar Babu, and V. Padmavathi, *Heteroatom Chem*., **12**(3), 131 (2001).
[6] D. Bhaskar Reddy, M. V. Ramana Reddy, and V. Padmavathi, *Indian J. Chem*., **36B,** 923 (1997).
[7] D. Bhaskar Reddy, A. Somasekhar Reddy, and V. Padmavathi, *Phosphorus, Sulfur, & Silicon*, **122,** 143 (1997).
[8] D. Bhaskar Reddy, M. V. Ramana Reddy, and V. Padmavathi, *Indian J. Chem*., **37B,** 167 (1998).
[9] D. Bhaskar Reddy, A. Somasekhar Reddy, and V. Padmavathi, *J. Chem. Research (S)*, **784,** (1998).

[10] D. Bhaskar Reddy, M. V. Ramana Reddy, A. Padmaja, and V. Padmavathi, *Indian J. Heterocyl. Chem*., **7,** 259 (1998).
[11] D. Bhaskar Reddy, M. V. Ramana Reddy, and V. Padmavathi, *Synth. Commun*., **29**(4), 667 (1999).
[12] D. Bhaskar Reddy, M. V. Ramana Reddy, and V. Padmavathi, *Heteroatom Chem*., **10**(1), 17 (1999).
[13] D. Bhaskar Reddy, A. Balaiah, V. Padmavathi, and A. Padmaja, *Heterocyl. Commun*., **5**(3), 285 (1999).
[14] V. Padmavathi, A. Padmaja, and D. Bhaskar Reddy, *Indian J. Chem*., **38B,** 308 (1999).
[15] D. Bhaskar Reddy, A. Somasekhar Reddy, V. Padmavathi, and N. Chandrasekhar Babu, *Heterocycl. Commun*., **6**(3), 271 (2000).
[16] D. Bhaskar Reddy, A. Balaiah, V. Padmavathi, and A. Padmaja, *Synth. Commun*., (in press).
[17] V. Padmavathi, T. V. Ramana Reddy, K. Venugopal Reddy, K. Audisesha Reddy, and D. Bhaskar Reddy, *Indian J. Chem*., **40B,** 667 (2001).
[18] I. Lalezari and A. Shafiee, *Tet. Lett*., **58,** 5105 (1969).
[19] C. D. Hurd and R. I. Mori, *J. Am. Chem. Soc*., **77,** 5359 (1955).
[20] J. P. Majoral, *Synthesis*, 557 (1978).