# Regioselectivity in Diels-Alder Reactions of Thiazolo[3,2-*d*][1,4,2]diazaphospholes and Related Compounds

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Z. Naturforsch. **60b,** 7 – 14 (2005); received July 13, 2004

Thiazolo[3,2-*d*][1,4,2]diazaphospholes as well as their 5,6-dihydro and benzo derivatives undergo Diels-Alder reactions at the >C=P– functionalities with 2,3-dimethylbutadiene and with isoprene. 1,3-Azaphospholo[5,1-*b*]benzothiazole, however, exhibits reduced reactivity and reacts with 1,3-dienes only in the presence of an oxidising agent ($O_2$, $S_8$ or $Se_n$). Reactions with isoprene occur regioselectively.

*Key words:* Regioselectivity, Diels-Alder Reaction, Thiazolo[3,2-*d*][1,4,2]diazaphospholes, 1,4,2-Diazaphospholo[5,4-*b*]benzothiazoles, 1,3-Azaphospholo[5,1-*b*]benzothiazole

## Introduction

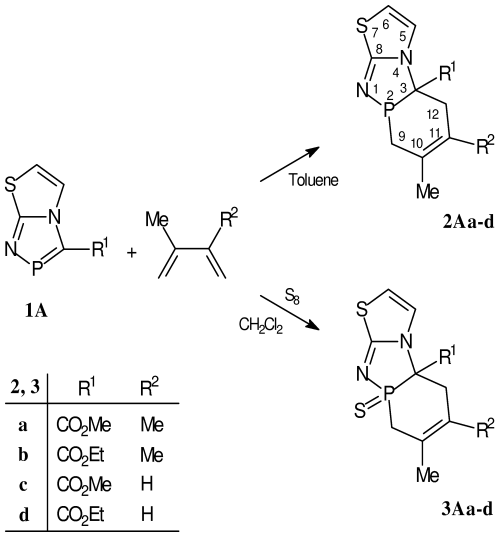
During the last few years the potential of the >C=P– functionality present in several classes of organophosphorus compounds, namely phosphaalkenes [1 – 3], heterophospholes including anellated azaphospholes [4 – 11] and phosphinines [12], to undergo Diels-Alder (DA) reactions has been recognised. Many such reactions using these compounds as dienophiles [4 – 7, 10 – 13] have been reported. In fact these reactions are found to occur much more readily than across the corresponding >C=C< moieties present in their carbocyclic analogues. This is in accordance with theoretical results showing that the presence of a two-coordinate phosphorus atom ($\sigma^2\lambda^3$-P) in a DA reactant lowers the activation energy relative to that of the hydrocarbon system due to the weakness of the >C=P–$\pi$ bond compared to the >C=C< $\pi$ bond [14, 15].

The DA reactions involving >C=P– as well as >C=C< functionalities, are stereoselective and regioselective. 2-Acetyl-1,2,3-diazaphosphole has been reported to react with isoprene with complete regioselectivity [16] whereas its reaction with cyclopentadiene gives an *endo* product which in solution subsequently changes to the *exo* product through cycloreversion [17]. We recently reported on the regioselectivity found in DA reactions of 1,3-bis(ethoxycarbonyl)-1,3-azaphospholo[5,1-*a*]isoquinoline with isoprene [18 – 20]. The calculations of the model DA reaction of phosphaethene with isoprene at the DFT level (B3LYP/6-311+G**) indicate the possibility of a radical cation mechanism, instead of a closed shell pericyclic mechanism, to account for the observed high regioselectivities [15].

## Results and Discussion

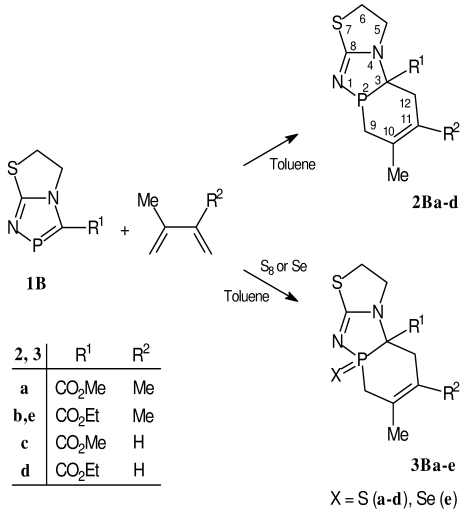
We have now investigated the DA reactions of thiazolo[3,2-*d*][1,4,2]diazaphospholes **1A** and their dihydro **1B** and benzo derivatives **1C** as well as those of 1,3-azaphospholo[5,1-*b*]benzothiazole **5** with 2,3-dimethylbutadiene and with isoprene; the detailed results, preliminarily mentioned in two reviews [6,13], are reported here.

3-Alkoxycarbonylthiazolo[3,2-*d*][1,4,2]diazaphospholes [21] **1A** react with 2,3-dimethylbutadiene and with isoprene to form [2+4] cycloadducts **2Aa – d**. As indicated by the $^{31}$P NMR spectra ($\delta^{31}$P ~ 84) of the reaction mixture, the reaction is complete within 4 h at ambient temperature. However the isolated cycloadducts were always contaminated with the corresponding oxides due to rapid oxidation of the three-coordinate phosphorus atoms during work up. When the reaction was carried out in presence of sulfur, the cycloadducts **2Aa – d** were converted into



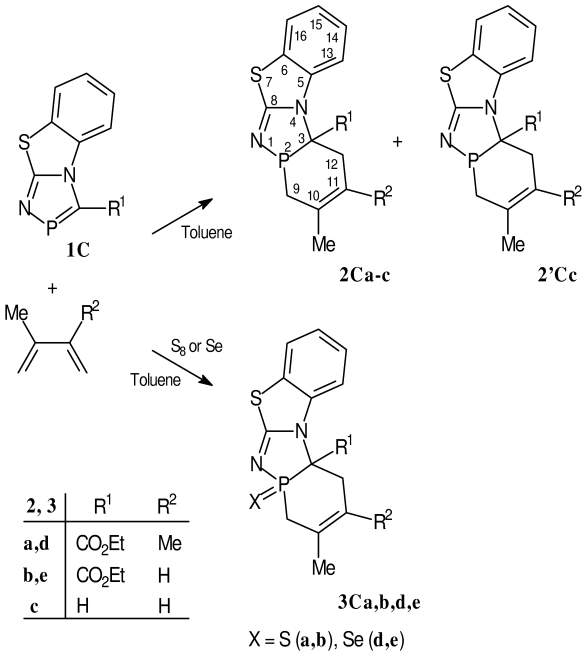

| 2, 3 | $R^1$ | $R^2$ |
|---|---|---|
| a | $CO_2Me$ | Me |
| b | $CO_2Et$ | Me |
| c | $CO_2Me$ | H |
| d | $CO_2Et$ | H |

Scheme 1.



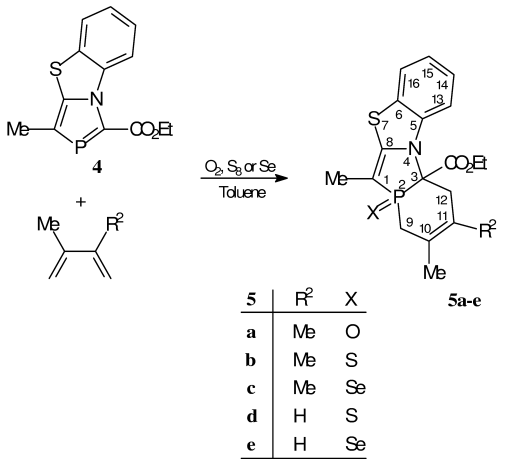

| 2, 3 | $R^1$ | $R^2$ |
|---|---|---|
| a | $CO_2Me$ | Me |
| b,e | $CO_2Et$ | Me |
| c | $CO_2Me$ | H |
| d | $CO_2Et$ | H |

Scheme 2.




| 2, 3 | $R^1$ | $R^2$ |
|---|---|---|
| a,d | $CO_2Et$ | Me |
| b,e | $CO_2Et$ | H |
| c | H | H |

Scheme 3.




| 5 | $R^2$ | X |
|---|---|---|
| a | Me | O |
| b | Me | S |
| c | Me | Se |
| d | H | S |
| e | H | Se |

Scheme 4.

the sulfides **3Aa – d** (Scheme 1), which were obtained in pure state. In the reaction with isoprene only one regioisomer was detected in the reaction mixture by $^{31}P$ NMR in each case.

3-Alkoxycarbonyl-5,6-dihydrothiazolo[3,2-*d*][1,4, 2]diazaphospholes [21] **1B** and 1,4,2-diazaphospholo[5,4-*b*]benzothiazoles [21] **1C** show similar behavior and give the [2+4] cycloadducts **2Ba – d** and **2Ca, b** (Scheme 2 and 3), respectively, which could be isolated in pure state. In these cases also the reaction with isoprene occurs with complete regioselectivity, except in the case of **1C** ($R^1 = H$) when the two regioisomers **2Cc** and **2'Cc** are formed in a 2:1 ratio, as indicated by $^{31}P$ NMR of the reaction mixture. On carrying out the reaction in the presence of sulfur or selenium, the corresponding sulfides **3Ba – d** and **3Ca, b** as well as the selenides **3Be** and **3Cd, e** are obtained.

3-Ethoxycarbonyl-1-methyl[1,3]azaphospholo[5,1-*b*]benzothiazole [22] **4** is less reactive and does not react with 2,3-dimethylbutadiene alone even on refluxing in toluene for several hours. The reaction,

Table 1. Physical and $^{31}$P NMR spectroscopic data of compounds **2**,**3** and **5**.

| Product | $R^1$ | $R^2$ | X | Yield [%] | M. p. [°C] | Molecular formula | $^{31}$P NMR[a] $\delta$ |
|---|---|---|---|---|---|---|---|
| **2Ba** | $CO_2Me$ | Me | – | 48 | 78 – 80 | $C_{12}H_{17}N_2O_2PS$ (284.3) | 83.9 |
| **2Bb** | $CO_2Et$ | Me | – | 44 | 82 – 84 | $C_{13}H_{19}N_2O_2PS$ (298.3) | 83.5 |
| **2Bc** | $CO_2Me$ | H | – | 44 | 85 – 87 | $C_{11}H_{15}N_2O_2PS$ (270.3) | 83.1 |
| **2Bd** | $CO_2Et$ | H | – | 41 | 80 – 82 | $C_{12}H_{17}N_2O_2PS$ (284.3) | 82.8 |
| **2Ca** | $CO_2Et$ | Me | – | 58 | 110 – 11 | $C_{17}H_{19}N_2O_2PS$ (346.4) | 84.0 |
| **2Cb** | $CO_2Et$ | H | – | 63 | 104 – 5 | $C_{16}H_{17}N_2O_2PS$ (332.4) | 82.5 |
| **2Cc+2'Cc** | H | H | – | – | – | $C_{13}H_{13}N_2PS$ (260.3) | 79.9, 80.3 |
| **3Aa** | $CO_2Me$ | Me | S | 41 | 178 – 80 | $C_{12}H_{15}N_2O_2PS_2$ (314.4) | 118.5 |
| **3Ab** | $CO_2Et$ | Me | S | 13 | 161 – 63 | $C_{13}H_{17}N_2O_2PS_2$ (328.4) | 118.2 |
| **3Ac** | $CO_2Me$ | H | S | 43 | 157 – 59 | $C_{11}H_{13}N_2O_2PS_2$ (300.3) | 114.3 |
| **3Ad** | $CO_2Et$ | H | S | 13 | 155 – 58 | $C_{12}H_{15}N_2O_2PS_2$ (314.4) | 114.8 |
| **3Ba** | $CO_2Me$ | Me | S | 53 | 174 – 75 | $C_{12}H_{17}N_2O_2PS_2$ (316.4) | 120.6 |
| **3Bb** | $CO_2Et$ | Me | S | 45 | 165 – 67 | $C_{13}H_{19}N_2O_2PS_2$ (330.4) | 121.5 |
| **3Bc** | $CO_2Me$ | H | S | 51 | 154 – 55 | $C_{11}H_{15}N_2O_2PS_2$ (302.4) | 119.8 |
| **3Bd** | $CO_2Et$ | H | S | 48 | 158 – 60 | $C_{12}H_{17}N_2O_2PS_2$ (316.4) | 118.2 |
| **3Be** | $CO_2Et$ | Me | Se | 40 | Syrupy | $C_{13}H_{19}N_2O_2PSSe$ (377.3) | 113.4 |
| **3Ca** | $CO_2Et$ | Me | S | 73 | 131 – 32 | $C_{17}H_{19}N_2O_2PS_2$ (378.5) | 119.6 |
| **3Cb** | $CO_2Et$ | H | S | 70 | 90 – 91 | $C_{16}H_{17}N_2O_2PS_2$ (364.4) | 118.4 |
| **3Cd** | $CO_2Et$ | Me | Se | 62 | Syrupy | $C_{17}H_{19}N_2O_2PSSe$ (425.3) | 112.5[b] |
| **3Ce** | $CO_2Et$ | H | Se | 59 | 122 – 23 | $C_{16}H_{17}N_2O_2PSSe$ (411.3) | 111.8[c] |
| **5a** | – | Me | O | 61 | 174 – 75 | $C_{19}H_{22}NO_3PS$ (375.4) | 74.0 |
| **5b** | – | Me | S | 75 | 110 – 11 | $C_{19}H_{22}NO_2PS_2$ (391.5) | 89.5 |
| **5c** | – | Me | Se | 55 | 146 – 48 | $C_{19}H_{22}NO_2PSSe$ (438.4) | 77.9[d] |
| **5d** | – | H | S | 71 | 139 – 40 | $C_{18}H_{20}NO_2PS_2$ (377.5) | 87.4 |
| **5e** | – | H | Se | 45 | 112 – 13 | $C_{18}H_{20}NO_2PSSe$ (424.4) | 72.0 |

[a] In $CDCl_3$; [b] $^1J_{SeP} = 826.3$ Hz; [c] $^1J_{SeP} = 846.8$ Hz; [d] $^1J_{SeP} = 758.2$ Hz.

however, occurs in the presence of an oxidising agent ($O_2$, $S_8$ or $Se_n$) to give the [2+4] cycloadducts **5** with a $\sigma^4\lambda^5$-phosphorus atom. Also in this case the reaction with isoprene proceeds with complete regioselectivity. Surprisingly **4** does not react with isoprene in the presence of oxygen (Scheme 4).

The role of the oxidising agent in the above reactions appears to be the shifting of a reversible Diels-Alder reaction between the azaphosphole ring and a diene in the forward direction by oxidising $\sigma^3$-P of the [2+4] cycloadduct formed initially in low concentration. A similar action of sulfur in the Diels-Alder reaction of 1,3-azaphospholo[5,1-*a*]isoquinoline was established recently [19].

All isolated products are colorless to pale yellow crystalline solids except **3Be** and **3Cd**, which are obtained as syrupy masses. They are soluble in polar organic solvents like chloroform and acetonitrile. All the compounds are spectroscopically pure and the assigned structures are supported by their $^{31}$P, $^1$H and $^{13}$C NMR data. Assignment of the $^1$H and $^{13}$C NMR data is based on $^1$H,$^1$H-COSY45, $^1$H,$^1$H-NOESY and $^1$H,$^{13}$C-HETCOR experiments performed on selected cycloadducts. The physical data and $^{31}$P NMR chemical shifts of the products are given in Table 1; $^{13}$C NMR data are shown in Table 2.

The Diels-Alder reactions across the >C=P– unit of the azaphosphole ring of thiazolo[3,2-*d*][1,4,2]diazaphospholes and the related systems lead to an increase in the coordination number at the phosphorus atoms and are accompanied by an upfield shift in the $^{31}$P NMR signals, which lie in the range $\delta = 112 - 122$ for **3** and $\delta = 72 - 90$ for **5** characteristic for a four-coordinate phosphorus atom [23]. The $^{31}$P NMR chemical shifts for the cycloadducts **2B** and **2C**, having a three-coordinate phosphorus atom, are found at $\delta = 80 - 84$, which is in accord with earlier results [24].

In the azaphospholes **1** the phosphorus atoms as well as the carbon atoms of the >C=P– moieties represent prochiral centres and thus the cycloaddition of the diene to this functionality leads in one step to the generation of two asymmetric centres. In the cycloadducts **2**, **3** and **5** the protons of the two methylene groups in the anellated phosphinine ring are diastereotopic, which becomes clearly visible in the $^1$H NMR spectra (see Experimental Section). Interestingly, the diastereotopy is more pronounced for the protons at C-12 compared to that at C-9. In the case of the dihydrothiazolo derivatives **2B** and **3B** the protons of the two methylene groups in the thiazoline ring also show the expected diastereotopy.

| $\delta, J$ [Hz] | **2Ca** | **2Cb** | **3Aa** | **3Ba** | **3Bb** | **3Bc** | **3Bd** | **3Ca** | **3Cb** | **3Cd** | **3Ce** | **5b** | **5c** | **5d** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C-1 | – | – | – | – | – | – | – | – | – | – | – | 79.4 | 78.4 | 79.5 |
| $^1J_{PC}$ | – | – | – | – | – | – | – | – | – | – | – | 80.5 | 71.1 | 80.6 |
| C-3 | 62.1 | 62.2 | 69.0 | 68.9 | 68.4 | 68.5 | 68.5 | 67.3 | 67.5 | 68.5 | 68.5 | 68.7 | 69.0 | 69.0 |
| $^1J_{PC}$ | 62.6 | 62.6 | 44.8 | 45.5 | 45.5 | 45.0 | 45.0 | 45.5 | 44.1 | 36.0 | 35.6 | 54.0 | 47.0 | 53.1 |
| C-5 | 135.3 | 134.9 | 122.2 | 45.1 | 45.8 | 45.0 | 44.9 | 135.1 | 134.8 | 134.9 | 134.5 | 138.5 | 138.4 | 138.4 |
| $^3J_{PC}$ | 7.6 | 7.6 | 6.3 | 4.7 | 4.7 | 5.2 | 5.7 | 7.1 | 7.1 | 6.5 | 6.5 | 4.2 | 4.0 | 4.3 |
| $^1J_{CH}$ | – | – | 191.7 | – | – | 146.1 | 147.9 | – | – | – | – | – | – | – |
| $^2J_{CH}$ | – | – | 6.3 | – | – | – | 3.4 | – | – | – | – | – | – | – |
| C-6 | 123.3 | 123.7 | 103.5 | 30.4 | 30.5 | 30.2 | 30.3 | 123.5 | 124.0 | 123.8 | 124.1 | 134.8 | 135.0 | 125.0 |
| $^1J_{CH}$ | – | – | 197.6 | – | – | 148.0 | 147.3 | – | – | – | – | – | – | – |
| $^2J_{CH}$ | – | – | 8.7 | – | – | 4.6 | 4.4 | – | – | – | – | – | – | – |
| C-8 | 166.1 | 166.2[a] | 167.8 | 168.0 | 167.5 | 168.3[b] | 167.6 | 166.5 | 166.6 | 166.9 | 166.8 | 173.5 | 173.6 | 166.8 |
| C-9 | 33.2 | 32.1 | 41.6 | 41.4 | 41.9 | 40.4 | 40.4 | 41.5 | 40.8 | 43.3 | 42.5 | 40.5 | 42.3 | 39.3 |
| $^1J_{PC}$ | 81.5 | 81.5 | 59.0 | 56.9 | 56.9 | 56.4 | 56.4 | 58.3 | 58.3 | 48.3 | 47.8 | 48.2 | 40.0 | 48.0 |
| $^1J_{CH}$ | – | – | 132.8 | – | – | 132.9 | 137.1 | – | – | 133.8 | 136.8 | – | – | – |
| $^3J_{CH}$ | – | – | 4.5 | – | – | 4.4,8.5 | 4.0 | – | – | 4.7 | 4.1 | – | – | – |
| C-10 | 125.8 | 134.6 | 125.6 | 125.8 | 125.5 | 135.7 | 135.6 | 126.5 | 135.4 | 126.8 | 135.5 | 126.3 | 126.4 | 134.6 |
| $^2J_{PC}$ | 12.3 | 9.5 | – | 11.8 | 11.9 | 11.4 | 11.4 | 12.3 | 11.9 | 12.3 | 12.3 | – | – | 10.9 |
| $^2J_{CH}$ | – | – | – | – | – | | – | – | – | 5.7 | 5.8 | – | – | – |
| C-11 | 124.4 | 118.4 | 126.2 | 126.0 | 125.8 | 118.5 | 118.1 | 125.3 | 119.1 | 125.8 | 119.2 | 125.6 | 125.3 | 120.1 |
| $^3J_{PC}$ | 10.4 | 13.3 | – | 12.3 | 11.9 | 12.8 | 12.3 | 12.3 | 12.8 | 13.3 | 12.9 | 11.5 | 12.5 | 12.8 |
| $^1J_{CH}$ | – | – | – | – | – | 161.6 | 173.6 | – | – | – | 167.2 | – | – | – |
| $^2J_{CH}/^3J_{CH}$ | – | – | – | – | – | | 6.1 | – | – | – | 6.1,1.7 | – | – | – |
| C-12 | 35.7 | 28.4 | 38.8 | 36.3 | 36.5 | 28.6 | 28.7 | 35.4 | 28.3 | 35.4 | 28.2 | 35.2 | 35.3 | 29.3 |
| $^2J_{PC}$ | – | – | – | 1.4 | 1.4 | 1.4 | 1.0 | 1.0 | – | – | 1.3 | 1.8 | 1.5 | – |
| $^1J_{CH}$ | – | – | 132.1 | – | – | 132.7 | 132.8 | – | – | 134.4 | 135.4 | – | – | – |
| $^2J_{CH}/^3J_{CH}$ | – | – | 4.6 | – | – | 4.6 | 4.9 | – | – | 4.7 | 5.6 | – | – | – |
| C-13 | 123.5 | 123.5 | – | – | – | – | – | 123.4 | 123.5 | 123.5 | 123.5 | 122.6 | 122.4 | 122.7 |
| $^1J_{CH}$ | – | – | – | – | – | – | – | – | – | 164.2 | 164.2 | – | – | – |
| $^3J_{CH}$ | – | – | – | – | – | – | – | – | – | 7.4 | 7.8 | – | – | – |
| C-14 | 127.1 | 127.0 | – | – | – | – | – | 127.0 | 127.0 | 127.1 | 127.0 | 121.4 | 121.5 | 126.4 |
| $^1J_{CH}$ | – | – | – | – | – | – | – | – | – | 163.0 | 162.9 | – | – | – |
| $^3J_{CH}$ | – | – | – | – | – | – | – | – | – | 7.6 | 7.8 | – | – | – |
| C-15 | 123.5 | 123.5 | – | – | – | – | – | 123.4 | 123.5 | 123.5 | 123.5 | 120.6 | 120.8 | 120.7 |
| $^1J_{CH}$ | – | – | – | – | – | – | – | – | – | 164.2 | 164.2 | – | – | – |
| $^3J_{CH}$ | – | – | – | – | – | – | – | – | – | 7.4 | 7.8 | – | – | – |
| C-16 | 110.2 | 110.3 | – | – | – | – | – | 110.0 | 110.2 | 110.1 | 110.2 | 124.4 | 124.7 | 108.0 |
| $^1J_{CH}$ | – | – | – | – | – | – | – | – | – | 162.5 | 162.3 | – | – | – |
| $^2J_{CH}/^3J_{CH}$ | – | – | – | – | – | – | – | – | – | 8.5 | 1.3,7.1 | – | – | – |
| 1-$CH_3$ | – | – | – | – | – | – | – | – | – | – | – | 8.8 | 9.3 | 8.8 |
| $^2J_{PC}$ | – | – | – | – | – | – | – | – | – | – | – | 9.4 | 10.1 | 9.5 |
| 10-$CH_3$ | 20.7 | 24.5 | 20.4 | 20.8 | 20.8 | 24.5 | 24.4 | 20.4 | 24.3 | 20.5 | 24.2 | 20.1 | 20.1 | 24.1 |
| $^3J_{PC}$ | 6.6 | 6.6 | – | 6.2 | 6.2 | 6.2 | 6.6 | 6.2 | 6.2 | 5.7 | 5.8 | 5.0 | 4.3 | 5.2 |
| $^1J_{CH}$ | – | – | 126.6 | – | – | 121.3 | 127.3 | – | – | 125.1 | 127.4 | – | – | – |
| $^3J_{CH}$ | – | – | – | – | – | 1.9 | 2.0 | – | – | 2.2 | – | – | – | – |
| 11-$CH_3$ | 20.1 | – | 20.6 | 20.5 | 20.7 | – | – | 20.0 | – | 20.2 | – | 20.0 | 20.1 | – |
| $^4J_{PC}$ | 3.8 | – | – | 3.8 | 3.3 | – | – | 3.8 | – | 3.8 | – | – | – | – |
| $^1J_{CH}$ | – | – | 126.5 | – | – | – | – | – | – | 126.1 | – | – | – | – |
| CO | 174.2 | 174.4 | 175.0 | 177.1 | 176.5 | 177.4 | 177.3 | 172.7 | 172.9 | 173.0 | 172.9 | 157.0 | 156.8 | 157.3 |
| $^2J_{PC}$ | 6.7 | 6.6 | 18.9 | 11.8 | 11.4 | 11.4 | 10.9 | 12.3 | 11.9 | 14.7 | 14.2 | 16.3 | 14.7 | 17.1 |
| $OCH_2/OCH_3$ | 62.9 | 63.0 | 53.5 | 53.2 | 62.6 | 53.2 | 62.6 | 62.8 | 63.0 | 63.0 | 63.0 | 62.5 | 62.7 | 62.7 |
| $^1J_{CH}$ | – | – | 148.4 | – | – | 148.2 | 149.3 | – | – | 148.9 | 148.8 | – | – | – |
| $^2J_{CH}$ | – | – | – | – | – | – | 4.5 | – | – | 4.4 | 4.5 | – | – | – |
| $CH_3$ | 14.1 | 14.1 | – | – | 14.4 | – | 14.4 | 14.2 | 14.3 | 14.3 | 14.2 | 14.2 | 14.2 | 14.2 |
| $^1J_{CH}$ | – | – | – | – | – | – | 150.3 | – | – | 127.5 | 127.4 | – | – | – |
| $^2J_{CH}$ | – | – | – | – | – | – | 4.9 | – | – | 2.6 | 2.6 | – | – | – |

Table 2. $^{13}$C-NMR data of cycloadducts **2**, **3** and **5** (in $CDCl_3$).

[a] $^2J_{PC} = 2.8$ Hz; [b] $^3J_{CH} = 4.3$ Hz.

The constitution of the cycloadducts **2**, **3** and **5** is further supported by the $^{13}$C NMR data (Table 2). The signals of the carbon atoms C-3 ($\delta = 62.1 - 69.0$) and C-9 ($\delta = 32.1 - 43.3$), which are directly bonded to the phosphorus atom, are readily identified by large values of $^1J_{PC}$. In the $\sigma^3\lambda^3$-cycloadducts **2** the coupling is larger (62.6 – 81.5 Hz) than in the sulfides **3** (35.6 – 59.0 Hz). $^2J_{PC}$ to C-12 in the phosphinine ring is small with values between 1.0 and 1.8 Hz. The same applies also to $^2J_{PC}$ of C-8 in the azaphosphole ring, which was resolved only in the case of **2Cb** (2.8 Hz). As expected, the P,C coupling to 10-$CH_3$ (4.3 – 6.6 Hz) over three bonds is larger than to 11-$CH_3$ (3.3 – 3.8 Hz) over four bonds.

## Conclusion

Thiazolo[3,2-*d*][1,4,2]diazaphospholes and related compounds as well as 1,3-azaphospholo[5,1-*b*]benzothiazoles undergo Diels-Alder reactions; however, the reactivities of the two systems differ appreciably: the former are more reactive and give the cycloaddition even in the absence of an oxidising agent, while the reaction of the latter occurs only in the presence of an oxidising agent. The reactions are stereo- and regioselective. The cycloadditions described herein are of interest as they can be used for the preparation of chiral phosphines.

## Experimental Section

*General:* All manipulations were carried out under an atmosphere of dry Ar or $N_2$ in flame dried glass apparatus. Toluene was kept over sodium wire for two days, distilled and stored over molecular sieves (4 Å). $CH_2Cl_2$ was refluxed over $P_2O_5$ for 1 h and distilled. 2,3-Dimethylbutadiene, isoprene, sulfur and selenium were purchased from Aldrich Chemical Co. and used without further purification. The azaphospholes, namely 3-alkoxycarbonylthiazolo[3,2-*d*][1,4,2]diazaphospholes **1A** [21], 3-alkoxycarbonyl-5,6-dihydrothiazolo[3,2-*d*][1,4,2]diazaphospholes **1B** [21], 1,4,2-diazaphospholo[5,4-*b*]benzothiazole **1C** [21] and 3-ethoxycarbonyl-1-methyl[1,3]azazphospholo[5,1-*b*]benzothiazole **4** [22] were prepared according to the methods reported earlier.

Melting points were determined with a Tempo melting point apparatus and are uncorrected. NMR spectra were recorded with a JEOL FX-90Q spectrometer operating at 89.55 MHz for $^1$H and 36.23 MHz for $^{31}$P and with a JEOL EX-400 spectrometer operating at 399.8 MHz for $^1$H and 100.5 MHz for $^{13}$C. $^1$H and $^{13}$C chemical shifts are given with respect to TMS as internal standard while $^{31}$P chemical shifts are referred to 85% $H_3PO_4$ as external standard.

*Typical procedure for the preparation of the [2+4] cycloadducts* **2Ba – d** *and* **2Ca – c***:* To a well stirred suspension of **1B** or **1C** (2 mmol) in toluene (15 ml) was added the 1,3-diene (2 mmol) and the reaction mixture was stirred at ambient temperature (20 °C) for 24 – 48 h. The progress of the reaction was monitored by $^{31}$P NMR. After the reaction was complete, the solution was filtered. In the case of **2Ba – d**, the filtrate was concentrated to *ca.* 10 ml and left in a refrigerator (−20 °C) whereby crystals were deposited. In the case of **2Ca – c** the filtrate was dried and the residue was extracted with $Et_2O$ (2 × 25 ml). The ether extract was concentrated to *ca.* 5 ml and left in the refrigerator whereby a colorless to pale yellow solid deposited. **2Cc** and **2'Cc** could not be separated and were obtained as a mixture.

**2Ba:** $^1$H NMR ($CDCl_3$): $\delta = 1.71$ (s, 6H, 10-$CH_3$ and 11-$CH_3$); AB part of ABX spin system ($\delta_A = 2.92$, $\delta_B = 2.57$, $^2J_{AB} = 17.8$ Hz, $^3J_{AX}$ and $^3J_{BX}$ not resolved, H-12); 2.88 (bs, 2H, H-9); 3.19 – 4.12 (m, 7H, H-5, H-6 and $OCH_3$).

**2Bb:** $^1$H NMR ($CDCl_3$): $\delta = 1.27$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.70 (s, 3H, 11-$CH_3$); 1.80 (s, 3H, 10-$CH_3$); AB part of ABX spin system ($\delta_A = 2.82$, $\delta_B = 2.25$, $^2J_{AB} = 17.1$ Hz, $^3J_{AX} = 17.3$ Hz, $^3J_{BX} = 17.1$ Hz, H-12); AB part of ABX spin system ($\delta_A = 2.60$, $\delta_B = 2.47$, $^2J_{AB} = 16.1$ Hz, $^3J_{AX} = 18.6$ Hz, $^3J_{BX} = 24.4$ Hz, H-9); 3.36 – 4.08 (m, 4H, H-5, H-6); AB part of $ABM_3X$ spin system ($\delta_A = 4.29$, $\delta_B = 4.26$, $^2J_{AB} = 10.7$ Hz, $^3J_{AX} = {}^3J_{BX} = 7.1$ Hz, $^5J_{AX} = 3.6$ Hz, $OCH_2$).

**2Bc:** $^1$H NMR ($CDCl_3$): $\delta = 1.79$ (s, 3H, 10-$CH_3$); AB part of ABX spin system ($\delta_A = 3.49$, $\delta_B = 2.91$, $^2J_{AB} = 14.5$ Hz, $^3J_{AX}$ and $^3J_{BX}$ not resolved, H-12); 3.12 (d, 2H, $^2J_{PH} = 13.6$ Hz, H-9); 3.20 – 3.35 (m, 2H, H-5); 3.80 (s, 3H, $OCH_3$); 3.89 – 4.03 (m, 2H, H-6); 5.42 (bs, 1H, H-11).

**2Bd:** $^1$H NMR ($CDCl_3$): $\delta = 1.28$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.76 (s, 3H, 10-$CH_3$); AB part of ABMX spin system ($\delta_A = 2.83$, $\delta_B = 2.61$, $^2J_{AB} = 15.9$ Hz, $^3J_{AX} = 16.1$ Hz, $^3J_{BX} = 26.9$ Hz, $^3J_{AM} = 7.6$ Hz, H-12; AB part of ABX spin system ($\delta_A = 2.75$, $\delta_B = 2.72$, $^2J_{AB} = {}^2J_{AX} = 18.6$ Hz, $^2J_{BX} = 19.3$ Hz, H-9); 3.39 – 3.96 (m, 4H, H-5, H-6); 4.30 (q, 2H, $^3J_{HH} = 7.1$ Hz, $OCH_2$); 5.37 (m, 1H, H-11).

**2Ca:** $^1$H NMR ($CDCl_3$): $\delta = 1.18$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.34 (d, 3H, $^5J_{PH} = 4.4$ Hz, 11-$CH_3$); 1.70 (s, 3H, 10-$CH_3$); AB part of ABX spin system ($\delta_A = 3.48$, $\delta_B = 2.72$, $^2J_{AB} = 15.8$ Hz, $^3J_{AX} = 15.6$ Hz, $^3J_{BX} = 18.3$ Hz, H-12); 2.96 (d, 2H, $^2J_{PH} = 26.0$ Hz, H-9); 4.21-4.36 (m, 2H, $OCH_2$); 6.86 (dd, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.1$ Hz, H-16); 7.16 (ddd, 1H, $^3J_{HH} = 7.7$ Hz, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 1.1$ Hz, H-14); 7.30 (td, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.3$ Hz, H-15); 7.46 (dd, 1H, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 1.3$ Hz, H-13). – $C_{17}H_{19}N_2O_2PS$ (346.4): calcd. C 58.95, H 5.53, N 8.09; found C 58.70, H 5.12, N 8.25.

**2Cb:** $^1$H NMR ($CDCl_3$): $\delta = 1.18$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.75 (s, 3H, 10-$CH_3$); 2.72 – 3.36 (m, 4H, H-9 and H-12); 4.11 – 4.35 (m, 2H, $OCH_2$); 5.26 (bs, 1H, H-11), 6.81 (dd, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.0$ Hz, H-16); 7.16 (td, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.3$ Hz, H-14); 7.29 (td, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.4$ Hz, H-15); 7.47 (dd, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.3$ Hz, H-13). – $C_{16}H_{17}N_2O_2PS$ (332.4): calcd. C 57.82, H 5.16, N 8.43; found C 57.28, H 5.38, N 8.29.

*Typical procedure for the preparation of the [2+4] cycloadducts* **3Aa** – **d***:* To a well stirred suspension of **1A** (1 mmol) in $CH_2Cl_2$ (10 ml) were added the 1,3-diene (1 mmol) and sulfur (0.032 g, 1 mmol) or selenium (0.079 g, 1 mmol) and the reaction mixture was stirred at ambient temperature (20 °C) for 24 – 35 h. After the reaction was complete ($^{31}$P NMR), the solution was filtered and the filtrate was concentrated to *ca.* 5 ml and left in a refrigerator (−20 °C) whereby a colorless to pale yellow solid deposited.

**3Aa:** $^1$H NMR ($CDCl_3$): $\delta = 1.58$ (d, 3H, $^5J_{PH} = 5.5$ Hz, 11-$CH_3$); 1.73 (s, 3H, 10-$CH_3$); AB part of ABX spin system ($\delta_A = 3.35$, $\delta_B = 2.63$, $^2J_{AB} = 15.5$ Hz, $^3J_{AX} = 16.0$ Hz, $^3J_{BX} = 25.4$ Hz, H-12); AB part of ABX spin system ($\delta_A = 2.96$, $\delta_B = 2.92$, $^2J_{AB} = ^2J_{AX} = ^2J_{BX} = 15.7$ Hz, H-9); 3.83 (s, 3H, $OCH_3$); 6.10 (dd, 1H, $^3J_{HH} = 4.8$ Hz, $^5J_{PH} = 5.7$ Hz, H-6); 6.68 (d, 1H, $^3J_{HH} = 4.8$ Hz, H-5). – $C_{12}H_{15}N_2O_2PS_2$ (314.4): calcd. C 45.85, H 4.81, N 8.91; found C 45.38, H 4.62, N 8.47.

**3Ab:** $^1$H NMR ($CDCl_3$): $\delta = 1.30$ (t, 3H, $^3J_{HH} = 8.0$ Hz, $OCH_2CH_3$); 1.56 (d, 3H, $^5J_{PH} = 6.0$ Hz, 11-$CH_3$); 1.70 (s, 3H, 10-$CH_3$); AB part of ABX spin system ($\delta_A = 3.35$, $\delta_B = 2.55$, $^2J_{AB} = 16.0$ Hz, $^3J_{AX} = 16.0$ Hz, $^3J_{BX} = 24.0$ Hz, H-12); AB part of ABX spin system ($\delta_A = 3.03$, $\delta_B = 2.86$, $^2J_{AB} = ^2J_{AX} = ^2J_{BX} = 16.0$ Hz, H-9); 4.33 (q, 3H, $^3J_{HH} = 8.0$ Hz, $OCH_2$); 6.20 (t, 1H, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 5.0$ Hz, H-6); 6.75 (d, 1H, $^3J_{HH} = 5.0$ Hz, H-5).

**3Ac:** $^1$H NMR ($CDCl_3$): $\delta = 1.74$ (s, 3H, 10-$CH_3$); AB part of ABX spin system ($\delta_A = 3.40$, $\delta_B = 2.68$, $^2J_{AB} = 16.0$ Hz, $^3J_{AX} = 16.0$ Hz, $^3J_{BX} = 20.0$ Hz, H-12); AB part of ABX spin system ($\delta_A = 3.08$, $\delta_B = 2.90$, $^2J_{AB} = ^2J_{AX} = ^2J_{BX} = 16.0$ Hz, H-9); 3.79 (s, 3H, $OCH_3$); 5.40 (bs, 1H, H-11); 6.34 (dd, 1H, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 5.0$ Hz, H-6); 6.79 (d, 1H, $^3J_{HH} = 5.0$ Hz, H-5).

**3Ad:** $^1$H NMR ($CDCl_3$): $\delta = 1.30$ (t, 3H, $^3J_{HH} = 7.0$ Hz, $OCH_2CH_3$); 1.79 (s, 3H, 10-$CH_3$); AB part of ABX spin system ($\delta_A = 3.43$, $\delta_B = 2.68$, $^2J_{AB} = 16.0$ Hz, $^3J_{AX} = 16.0$ Hz, $^3J_{BX} = 22.0$ Hz, H-12); AB part of ABX spin system ($\delta_A = 3.43$, $\delta_B = 2.90$, $^2J_{AB} = ^2J_{AX} = ^2J_{BX} = 15.0$ Hz, H-9); 4.33 (q, 3H, $^3J_{HH} = 7.0$ Hz, $OCH_2$); 5.40 (s, 1H, H-11); 6.30 (t, 1H, $^3J_{HH} = 5.0$ Hz, $^5J_{PH} = 5.0$ Hz, H-6); 6.74 (d, 1H, $^3J_{HH} = 5.0$ Hz, H-5).

*Typical procedure for the preparation of the [2+4] cycloadducts* **3Ba** – **e***:* To a well stirred suspension of **1B** (2 mmol) in toluene (20 ml) were added the 1,3-diene (2 mmol) and sulfur (0.064 g, 2 mmol) or selenium (0.158 g, 2 mmol) and the reaction mixture was stirred at ambient temperature (20 °C) for 24 h. In the case of 2,3-dimethylbutadiene and sulfur the reaction was complete after heating to 40 °C for 2 h. The solution was filtered and the filtrate was evaporated to dryness. The residue was extracted with $Et_2O$ ($2 \times 25$ ml) and the ether extract was concentrated to *ca.* 5 ml and left in a refrigerator (−20 °C) whereby a colorless to pale yellow solid deposited.

**3Ba:** $^1$H NMR ($CDCl_3$): $\delta = 1.74$ (s, 6H, 10-$CH_3$ and 11-$CH_3$); AB part of ABX spin system ($\delta_A = 3.21$, $\delta_B = 2.57$, $^2J_{AB} = 15.7$ Hz, $^3J_{AX} = 14.9$ Hz, $^3J_{BX} = 26.1$ Hz, H-12); 2.88 (d, 2H, $^2J_{PH} = 15.1$ Hz, H-9); 3.43 (m, 1H, 6-H); 3.48 – 3.56 and 3.76 – 3.89 (m, 4H, 5-H and 6-H); 3.82 (s, 3H, $OCH_3$).

**3Bb:** $^1$H NMR ($CDCl_3$): $\delta = 1.32$ (t, 3H, $^3J_{HH} = 7.2$ Hz, $OCH_2CH_3$); 1.74 (s, 6H, 10-$CH_3$ and 11-$CH_3$); AB part of ABX spin system ($\delta_A = 3.19$, $\delta_B = 2.55$, $^2J_{AB} = 15.5$ Hz, $^3J_{AX} = 15.5$ Hz, $^3J_{BX} = 26.1$ Hz, H-12); 2.88 (d, 2H, $^2J_{PH} = 15.4$ Hz, H-9); AB part of $ABM_3X$ spin system ($\delta_A = 4.28$, $\delta_B = 4.25$, $^2J_{AB} = 19.1$ Hz, $^3J_{AM} = ^3J_{BM} = 7.2$ Hz, $^5J_{AX} = 3.6$ Hz, $OCH_2$); 3.41 (m, 1H, 5-H); 3.50 – 3.55 (m, 2H, H-6); 3.82 (m, 1H, 5-H).

**3Bc:** $^1$H NMR ($CDCl_3$): $\delta = 1.76$ (s, 3H, 10-$CH_3$); AB part of ABMX spin system ($\delta_A = 3.02$, $\delta_B = 2.67$, $^2J_{AB} = 16.1$ Hz, $^3J_{AX} = 16.1$ Hz, $^3J_{BX} = 23.7$ Hz, $^3J_{AM} = 6.1$ Hz, $^3J_{BM} = 8.0$ Hz, H-12); AB part of ABMX spin system ($\delta_A = 2.90$, $\delta_B = 2.84$, $^2J_{AB} = 16.0$ Hz, $^3J_{AX} = 16.0$ Hz, $^3J_{BX} = 15.1$ Hz, $^4J_{BM} = 2.0$ Hz, H-9); 3.36 – 3.72 (m, 4H, H-5 and H-6); 3.81 (s, 3H, $OCH_3$), 5.46 (ddd, $^3J_{HH} = 8.0$, 6.1 Hz, $^4J_{PH} = 4.0$ Hz, H-11).

**3Bd:** $^1$H NMR ($CDCl_3$): $\delta = 1.24$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.69 (s, 3H, 10-$CH_3$); AB part of ABMX spin system ($\delta_A = 2.94$, $\delta_B = 2.66$, $^2J_{AB} = 15.7$ Hz, $^3J_{AX} = 15.2$ Hz, $^3J_{BX} = 26.3$ Hz, $^3J_{BM} = 7.6$ Hz, H-12); AB part of ABX spin system ($\delta_A = 2.84$, $\delta_B = 2.78$, $^2J_{AB} = 16.1$ Hz, $^2J_{AX} = 16.2$ Hz, $^2J_{BX} = 15.1$ Hz, H-9); AB part of ABX spin system ($\delta_A = 3.69$, $\delta_B = 3.41$, $^2J_{AB} = 11.7$ Hz, $^4J_{AX} = 3.6$ Hz, $^4J_{BX} = 3.7$ Hz, couplings with 6-$CH_2$ not resolved, H-5); 3.50 – 3.60 (m, 2H, H-6); AB part of $ABM_3X$ system ($\delta_A = 4.29$, $\delta_B = 4.26$, $^2J_{AB} = 18.2$ Hz, $^3J_{AM} = ^3J_{BM} = 7.3$ Hz, $^5J_{AX} = 3.4$ Hz, $OCH_2$); 5.44 (bs, 1H, H-11). – $C_{12}H_{17}N_2O_2PS_2$ (316.4): calcd. C 45.55, H 5.42, N 8.85; found C 45.53, H 5.05, N 8.80.

**3Be:** $^1$H NMR ($CDCl_3$): $\delta = 1.26$ (t, 3H, $^3J_{HH} = 8.5$ Hz, $OCH_2CH_3$); 1.66 (s, 6H, 10-$CH_3$ and 11-$CH_3$); AB part of ABX spin system ($\delta_A = 3.09$, $\delta_B = 2.51$, $^2J_{AB} = 16.2$ Hz, $^3J_{AX} = 16.2$ Hz, $^3J_{BH} = 25.3$ Hz, H-12); 2.81 (d, 2H, $^2J_{PH} = 15.1$ Hz, H-9); 3.32 – 3.85 (m, 4H, H-5 and H-6); 4.26 – 4.52 (m, 2H, $OCH_2$).

*Typical procedure for the preparation of the [2+4] cycloadducts* **3Ca**, **b**, **d**, **e***:* To a solution of **1C** (1 mmol) in toluene (10 ml) were added the 1,3-diene (1 mmol) and sulfur

(0.032 g, 1 mmol) or selenium (0.079 g, 1 mmol). In the case of **3Ca, b**, the reaction mixture was heated to 60 °C for 3 d whereas reaction in other cases was complete after heating to 60 °C for 25 – 30 d. The reaction mixture was worked up as described above for **3Ba – e**. The compounds **3Ca, b, d, e** were obtained as colorless to pale yellow solids.

**3Ca:** $^1$H NMR ($CDCl_3$): $\delta = 1.21$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.35 (s, 3H, 11-$CH_3$); 1.71 (s, 3H, 10-$CH_3$); 2.97 (d, 2H, $^2J_{PH} = 15.7$ Hz, H-9); AB part of ABX spin system ($\delta_A = 3.33$, $\delta_B = 3.03$, $^2J_{AB} = 15.8$ Hz, $^3J_{AX} = 16.2$ Hz, $^3J_{BX} = 25.6$ Hz, H-12); 4.28 (q, 2H, $^3J_{HH} = 7.1$ Hz, $OCH_2$); 6.84 (dd, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 0.7$ Hz, H-16); 7.14 (td, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.1$ Hz, H-14); 7.29 (td, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.3$ Hz, H-15); 7.42 (dd, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.3$ Hz, H-13). – $C_{17}H_{19}N_2O_2PS_2$ (378.5): calcd. C 53.95, H 5.06, N 7.40; found C 53.18, H 5.14, N 7.61.

**3Cb:** $^1$H NMR ($CDCl_3$): $\delta = 1.20$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.76 (s, 3H, 10-$CH_3$); 2.89 – 3.36 (m, 4H, H-9 and H-12); 4.28 (q, 2H, $^3J_{HH} = 7.1$ Hz, $OCH_2$); 5.29 – 5.35 (m, 1H, H-11); 6.80 (dd, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 0.7$ Hz, H-16); 7.15 (td, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.2$ Hz, H-14); 7.28 (td, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.5$ Hz, H-15); 7.43 (dd, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.2$ Hz, H-13). – $C_{16}H_{17}N_2O_2PS_2$ (364.4): calcd. C 52.73, H 4.70, N 7.69; found C 52.64, H 4.46, N 7.67.

**3Cd:** $^1$H NMR ($CDCl_3$): $\delta = 1.21$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.36 (s, 3H, 11-$CH_3$); 1.73 (s, 3H, 10-$CH_3$); 3.07 (d, 2H, $^2J_{PH} = 14.7$ Hz, H-9); AB part of ABX spin system ($\delta_A = 3.29$, $\delta_B = 3.04$, $^2J_{AB} = 15.8$ Hz, $^3J_{AX} = 16.4$ Hz, $^3J_{BX} = 25.4$ Hz, H-12); 4.30 (q, 2H, $^3J_{HH} = 7.1$ Hz, $OCH_2$); 6.85 (d, 1H, $^3J_{HH} = 7.8$ Hz, H-16); 7.15 (t, 1H, $^3J_{HH} = 7.8$ Hz, H-14); 7.29 (t, 1H, $^3J_{HH} = 7.8$ Hz, H-15); 7.42 (d, 1H, $^3J_{HH} = 7.8$ Hz, H-13).

**3Ce:** $^1$H NMR ($CDCl_3$): $\delta = 1.23$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.79 (s, 3H, 10-$CH_3$); 3.07 – 3.36 (m, 4H, H-9 and H-12); 4.34 (qd, 2H, $^3J_{HH} = 7.1$ Hz, $^5J_{PH} = 2.6$ Hz, $OCH_2$); 5.38 (d, 1H, $^4J_{PH} = 5.9$ Hz, H-11); 6.85 (d, 1H, $^3J_{HH} = 7.8$ Hz, H-16); 7.20 (t, 1H, $^3J_{HH} = 7.8$ Hz, H-14); 7.33 (t, 1H, $^3J_{HH} = 7.8$ Hz, H-15); 7.48 (d, 1H, $^3J_{HH} = 7.8$ Hz, H-13). – $C_{16}H_{17}N_2O_2PSSe$ (411.3): calcd. C 46.72, H 4.17, N 6.81; found C 46.87, H 4.66, N 6.93.

*Typical procedure for the preparation of the [2+4] cycloadducts* **5a – e***:* To a mixture of **4** (0.277 g, 1 mmol) in toluene (15 ml) were added the 1,3-diene (1 mmol) and sulfur (0.032 g, 1 mmol) or selenium (0.079 g, 1 mmol). The reaction mixture was heated to 30 °C for 2 h and then the temperature was raised to 60 °C for 40 – 45 h. After completion of the reaction ($^{31}$P NMR) the reaction mixture was worked up as described above for **3Ba – e**. The compounds **5a – e** were obtained as colorless to pale yellow solids.

In order to carry out the reaction in the presence of oxygen, the toluene was first flushed with dry and $CO_2$-free air for about 20 min and then **4** and the 1,3-diene were reacted as described above.

**5a:** $^1$H NMR ($CDCl_3$): $\delta = 1.10$ (t, 3H, $^3J_{HH} = 7.3$ Hz, $OCH_2CH_3$); 1.38 (d, 3H, $^4J_{PH} = 3.4$ Hz, 11-$CH_3$); 1.63 (s, 3H, 10-$CH_3$); 1.74 (d, 3H, $^3J_{PH} = 12.7$ Hz, 1-$CH_3$); 2.66 – 3.13 (m, 4H, H-9 and H-12); 4.23 (qd, 2H, $^3J_{HH} = 7.3$ Hz, $^5J_{PH} = 3.6$ Hz, $OCH_2$); 6.44 – 7.20 (m, 4H, H-16, H-15, H-14 and H-13).

**5b:** $^1$H NMR ($CDCl_3$): $\delta = 1.14$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.43 (d, 3H, $^4J_{PH} = 1.8$ Hz, 11-$CH_3$); 1.65 (s, 3H, 10-$CH_3$); 1.72 (d, 3H, $^3J_{PH} = 14.2$ Hz, 1-$CH_3$); AB part of ABX spin system ($\delta_A = 3.03$, $\delta_B = 2.89$, $^2J_{AB} = 15.8$ Hz, $^2J_{AX} = 25.7$ Hz, $^2J_{BX}$ unresolved, H-9); AB part of ABX system ($\delta_A = 3.22$, $\delta_B = 2.80$, $^2J_{AB} = 15.8$ Hz, $^3J_{AX} = 16.1$ Hz, $^3J_{BX} = 11.7$ Hz, H-12); 4.20 (m, 2H, $OCH_2$); 6.50 (d, 1H, $^3J_{HH} = 7.6$ Hz, H-16); 6.84 (td, 1H, $^3J_{HH} = 7.6$, $^4J_{HH} = 1.0$ Hz, H-15); 7.07 (td, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.2$ Hz, H-14); 7.18 (dd, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.0$ Hz, H-13).

**5c:** $^1$H NMR ($CDCl_3$): $\delta = 1.17$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.44 (d, 3H, $^4J_{PH} = 1.7$ Hz, 11-$CH_3$); 1.69 (s, 3H, 10-$CH_3$); 1.70 (d, 3H, $^3J_{PH} = 14.5$ Hz, 1-$CH_3$); AB part of ABX spin system ($\delta_A = 3.17$, $\delta_B = 2.99$, $^2J_{AB} = 15.5$ Hz, $^2J_{AX} = 25.1$ Hz, $^2J_{BX} = 1.5$ Hz, H-9); AB part of ABX spin system ($\delta_A = 3.10$, $\delta_B = 2.91$, $^2J_{AB} = 15.6$ Hz, $^3J_{AX} = 9.7$ Hz, $^3J_{BX} = 10.8$ Hz, H-12); 4.40 (m, 2H, $OCH_2$); 6.50 (d, 1H, $^3J_{HH} = 7.6$ Hz, H-16); 6.88 (td, 1H, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.0$ Hz, H-15); 7.10 (td, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.2$ Hz, H-14); 7.21 (dd, 1H, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.2$ Hz, H-13).

**5d:** $^1$H NMR ($CDCl_3$): $\delta = 1.12$ (t, 3H, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$); 1.69 (s, 3H, 10-$CH_3$); 1.72 (d, 3H, $^3J_{PH} = 14.2$ Hz, 1-$CH_3$); 2.85 – 3.14 (m, 4H, H-9 and H-12); AB part of $ABM_3$ system ($\delta_A = 4.26$, $\delta_B = 4.17$, $^2J_{AB} = 10.6$ Hz, $^3J_{AM} = ^3J_{BM} = 7.1$ Hz, $OCH_2$); 5.40 (m, 1H, H-11); 6.44 (d, 1H, $^3J_{HH} = 7.7$ Hz, H-16); 6.83 (td, 1H, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.0$ Hz, H-15); 7.05 (td, 1H, $^3J_{HH} = 7.1$ Hz, $^4J_{HH} = 1.2$ Hz, H-14); 7.18 (dd, 1H, $^3J_{HH} = 7.1$ Hz, $^4J_{HH} = 1.0$ Hz, H-13). – $C_{18}H_{20}NO_2PS_2$ (377.5): calcd. C 57.28, H 5.34, N 3.71; found C 57.85, H 5.26, N 3.90.

**5e:** $^1$H NMR ($CDCl_3$): $\delta = 1.18$ (t, 3H, $^3J_{HH} = 7.6$ Hz, $OCH_2CH_3$); 1.33 (s, 3H, 10-$CH_3$); 1.65 (d, 3H, $^3J_{PH} = 14.7$ Hz, 1-$CH_3$); 2.78 – 3.62 (m, 4H, H-9 and H-12); 4.18 (qd, 2H, $^3J_{HH} = 7.6$ Hz, $^5J_{PH} = 3.8$ Hz, $OCH_2$); 5.54 (bs, 1H, H-11); 6.88-8.04 (m, 4H, H-16, H-15, H-14, H-13).

*Acknowledgements*

Financial support from the Department of Science and Technology, Government of India, New Delhi is gratefully acknowledged. Thanks are also due to the Alexander von Humboldt Foundation, Bonn.

[1] B. Weber, M. Regitz, in M. Regitz (ed): Methods in Organic Chemistry (Houben-Weyl), Vol. 4, part E1, p. 27, Thieme, Stuttgart (1982).
[2] L. N. Markovskii, V. D. Romanenko, Tetrahedron **45**, 6019 (1989).
[3] R. Appel, in M. Regitz, O. J. Scherer (eds): Multiple Bonds and Low Coordination in Phosphorus Chemistry, p. 157, Thieme, Stuttgart (1990).
[4] A. Schmidpeter, K. Karaghiosoff, in M. Regitz, O. J. Scherer (eds): Multiple Bonds and Low Coordination in Phosphorus Chemistry, p. 258, Thieme, Stuttgart (1990).
[5] A. Schmidpeter, in A. R. Katritzky, C. W. Rees, E. F. V. Scriven (eds): Comprehensive Heterocyclic Chemistry-II, Vol. 3, p. 709, 715; Vol. 4, p. 771, Pergamon, Oxford (1996).
[6] R. K. Bansal, K. Karaghiosoff, A. Schmidpeter, Tetrahedron **50**, 7675 (1994).
[7] A. Schmidpeter, in F. Mathey (ed): Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain, p. 363, Elsevier, Amsterdam (2001).
[8] R. K. Bansal, K. Karaghioshoff, N. Gandhi, A. Schmidpeter, Synthesis 361 (1995).
[9] R. K. Bansal, R. Mahnot, G. Pandey, R. Gupta, J. Indian Chem. Soc. **71**, 415 (1995).
[10] R. K. Bansal, N. Gupta, in R. C. Storr, T. L. Gilchrist (eds): Science of Synthesis: Methods of Molecular Transformations (Houben-Weyl), Vol. 13, p. 647, 689, 743, Thieme, Stuttgart (2004).
[11] R. K. Bansal, J. Heinicke, Chem. Rev. **101**, 3549 (2001).
[12] a) G. Märkl, in M. Regitz (ed): Methods in Organic Chemistry (Houben-Weyl), Vol. 4, Part E1, p. 72, Thieme, Stuttgart (1982); b) G. Märkl, in M. Regitz, O. J. Scherer (eds): Multiple Bonds and Low Coordination in Phosphorus Chemistry, p. 220, Thieme, Stuttgart (1990).
[13] R. K. Bansal, N. Gupta, N. Gupta, Heteroatom Chem. **15**, 271 (2004).
[14] S. M. Bachrach, M. Liu, J. Org. Chem. **57**, 6736 (1992).
[15] C. S. Wannere, R. K. Bansal, P. v. R. Schleyer, J. Org. Chem. **67**, 9162 (2002).
[16] R. Chen, B. Cai, G. Li, Synthesis, 783 (1991).
[17] Y. Y. C. Yeung Lam Ko, R. Carrie, L. Toupet, F. de Sarlo, Bull. Soc. Chim. Fr. 115 (1986).
[18] R. K. Bansal, L. Hemrajani, N. Gupta, Heteroatom Chem. **10**, 598 (1999).
[19] R. K. Bansal, V. K. Jain, N. Gupta, N. Gupta, L. Hemrajani, M. Baweja, P. G. Jones, Tetrahedron **58**, 1573 (2002).
[20] R. K. Bansal, A. Dandia, N. Gupta, D. Jain, Heteroatom Chem. **14**, 560 (2003).
[21] R. K. Bansal, R. Mahnot, D. C. Sharma, K. Karaghiosoff, Synthesis, 267 (1992).
[22] R. K. Bansal, R. Mahnot, D. C. Sharma, K. Karaghiosoff, A. Schmidpeter, Heteroatom Chem. **3**, 351 (1992).
[23] H. R. Hudson, K. B. Dillon, B. J. Walker, in J. C. Tebby (ed): CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data, p. 181, CRC, Boca Raton, FL (1991).
[24] L. Maier, P. J. Diel, J. C. Tebby, in J. C. Tebby (ed.): CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data, p. 121, CRC, Boca Raton, FL (1991).