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Tetrahedron 62 (2006) 7776–7782
Tetrahedron

Phosphonylated thiocarbonyl ylides from the reaction of aromatic thioketones with diethyl diazomethylphosphonates

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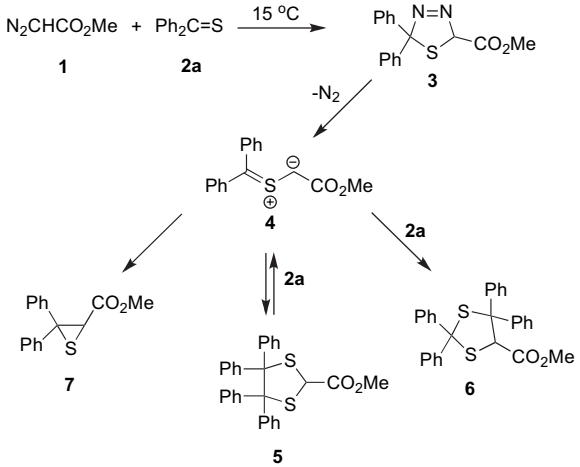
Received 20 April 2006; revised 16 May 2006; accepted 24 May 2006
Available online 16 June 2006

Abstract—The reaction of diazomethylphosphonates with aromatic thioketones at −65 °C to room temperature yields 2,5-dihydro-1,3,4-thiadiazole-2-phosphonates, which eliminates N_2 to give phosphonylated thiocarbonyl ylides as reactive intermediates. These sulfur-centered 1,3-dipoles undergo typical reactions of thiocarbonyl ylides, i.e., 1,3-dipolar cycloadditions, cyclodimerization, and electrocyclic ring closure, depending on the involved thioketone and, therefore, on the reaction conditions. In the case of the most reactive thiofluorenone, the phsophonylated thiocarbonyl methanide can be intercepted with thiobenzophenone, a phosphonodithioformate, and tetracyanoethylene. In the absence of such reactive dipolarophiles, cyclodimerization occurs to give the corresponding 1,4-dithiane.

1. Introduction

In contrast to the widely explored diazoacetates,[1] diazomethylphosphonates are rarely used in 1,3-dipolar cycloadditions. Only recently, reactions with imines to give 4,5-dihydro-1,2,3-thiazole-4-phosphonates or aziridine-2-phosphonates have been reported.[2] It is well established that reactions of diazo compounds with thiocarbonyl dipolarophiles lead to 2,5-dihydro-1,3,4-thiadiazoles, which offer a convenient access to reactive thiocarbonyl ylides.[3,4]

Diazoacetates were also applied in this reaction, even at a time when the reaction mechanism for the formation of thiiranes and 1,3-dithiolanes was not known.[5,6] The reaction of methyl diazoacetate (**1**) with thiobenzophenone (**2a**) was a key experiment in the elucidation of the reaction mechanism for the formation of 1,3-dithiolanes (so-called Schönberg products).[7] Interestingly, the regioisomeric 1,3-dithiolanes **5** and **6** were formed in a ratio of 1:1. The analogous reaction with 9*H*-fluorene-9-thione (**2b**) was reported to give the corresponding product of type **5** exclusively. Heating of the 'labile' isomer **5** to 100 °C resulted in the formation of a mixture of **6** and methyl 3,3-diphenylacrylate, which is the product of desulfurization of thiirane **7** (Scheme 1). The later reported reaction of diazoacetate with 9*H*-xanthene-9-thione (**2c**), which is less reactive than **2a**, in THF at 60 °C yielded only the corresponding acrylate.[8] In the same paper, the reaction of ethyl diazoacetate with sterically hindered cycloaliphatic thiones, derived from 2,2,4,4-tetramethylcyclobutane-1,3-dione, was reported to give only thiiranes. In a reaction of adamantanethione with ethyl



Scheme 1.

Keywords: Diazo compounds; Thioketones; Thiocarbonyl ylides; [2+3] Cycloadditions; Cyclodimerization; X-ray crystallography.
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† In part from the Ph.D. thesis of P.W., University of Łódź, 2004.

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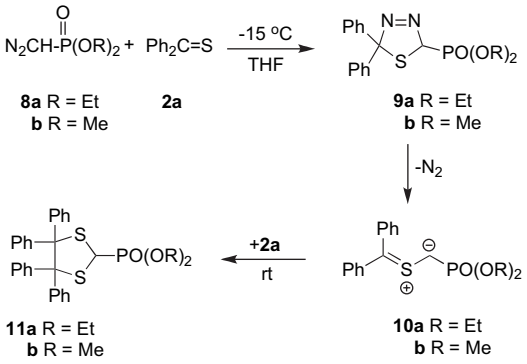
doi:10.1016/j.tet.2006.05.062

diazoacetate, which was catalyzed by $LiClO_4$, the sterically less hindered 1,3-dithiolane of type **6** was the sole product.[8] More complex reaction mixtures were obtained when ethyl diazoacetate was reacted with 4,4-disubstituted 1,3-thiazole-5(4*H*)-thiones.[9]

Phosphonylated thiocarbonyl ylides are attractive building blocks for the synthesis of phosphonylated sulfur heterocycles, which are difficult to access by other methods. Recently, these versatile dipolar species were generated from diazomethane and dialkyl phosphonodithioformates.[10,11] In the present paper, a different approach based on [2+3] cycloaddition of diazomethylphosphonates (**8**) with aromatic thioketones is described.

2. Results and discussion

Unlike the reaction with methyl diazoacetate (**1**, Scheme 1), the blue solution of thiobenzophenone (**2a**) in THF decolorized within ca. 30 min of the addition of an equimolar amount of **8a** at −15 °C, which indicates that **8a** is significantly more reactive than **1**. During the reaction, a slow evolution of nitrogen was observed. At room temperature, addition of **8a** to a solution of **2a** or vice versa was accompanied by a vigorous gas evolution. In the crude reaction mixture, a new product **11a** and unconsumed **8a** were found in a ratio of ca. 1:1 (^{1}H NMR). By trituration with hexane, **11a** was isolated as a colorless solid. Its structure was established as symmetrical 1,3-dithiolane on the basis of its ^{1}H and ^{13}C NMR spectra (Scheme 2). The most indicative signal is that for C(4) and C(5) appearing at 79.6 ppm ($^3J_{CP}$=7 Hz). The signal of C(2), which bears the phosphonate group, is located at 40.8 ppm as a doublet with $^1J_{CP}$=150.9 Hz. An analogous result was obtained in the case of dimethyl diazomethylphosphonate (**8b**).



Scheme 2.

Finally, the structure of **11a** was established by X-ray crystallography (Fig. 1). The five-membered heterocycle has a half-chair conformation twisted on S(1)–C(5). One ethyl group is disordered over two conformations.

In comparison with the result obtained with **1** (Scheme 1), the most important difference is that only the sterically more congested 1,3-dithiolane was formed, i.e., the [2+3] cycloaddition of **10** with **2a** occurs with high regioselectivity.

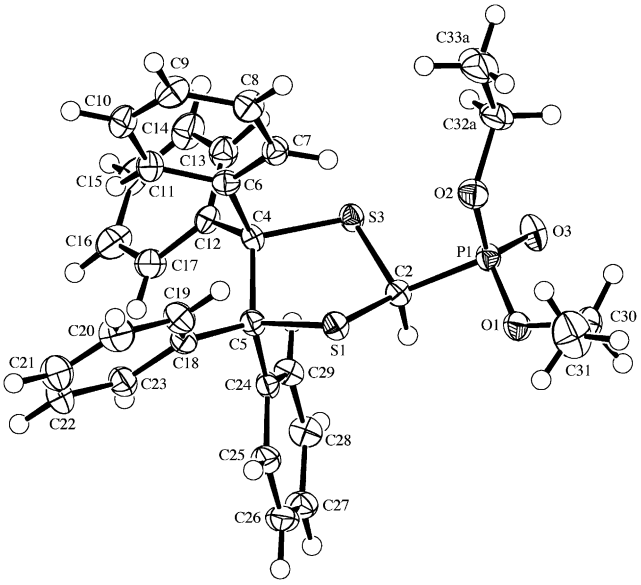


Figure 1. ORTEP-plot[13] of the molecular structure (conformation A) of **11a** (arbitrary numbering of atoms, 50% probability ellipsoids).

According to the reactivity scale elaborated for the [2+3] cycloaddition of diphenyldiazomethane and C=S dipolarophiles, 9*H*-fluoren-9-thione (**2b**) is approximately 100× more reactive than **2a**.[12] The enhanced reactivity of **2b** was confirmed in the reaction with **8a**. The decolorization of the 1:1 mixture occurred smoothly at −65 °C without evolution of nitrogen. The evolution of N_2 started between −50 and −45 °C, and after warming to room temperature, the crude mixture showed the presence of a single product (^{1}H NMR), with a characteristic signal at 4.84 ppm ($^2J_{HP}$=24.9 Hz, $^3J_{HP}$=12.6 Hz). The integration of this signal, which originates from **8a**, and the aromatic protons reveals a ratio of 1:8, which indicates that the starting materials reacted in a 1:1 ratio. The elemental analysis was in accordance with the values for the thiocarbonyl ylide **10c**, while the CIMS showed the $[M+1]^+$ peak at *m/z* 693. Therefore, the isolated product is a dimer of **10c**. Finally, the structure of the compound was established by X-ray crystallography (Fig. 2) as *trans*-1,4-dithiane-2,3-diphosphonate **12** (Scheme 3). The six-membered heterocycle

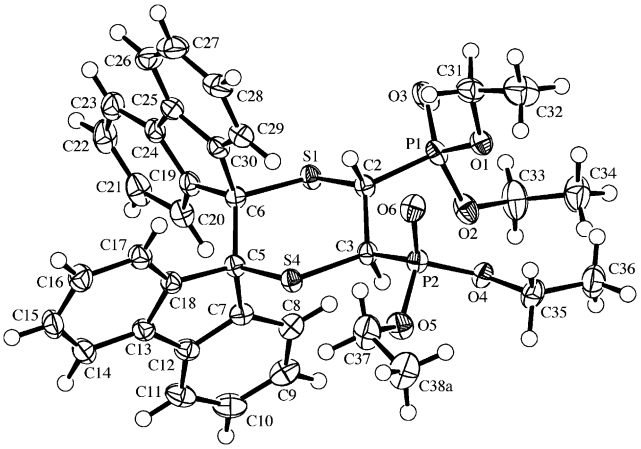
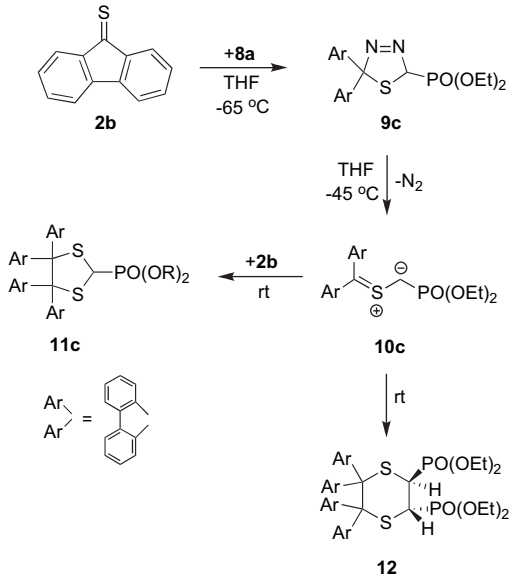


Figure 2. ORTEP-plot[13] of the molecular structure (conformation A) of **12** (arbitrary numbering of atoms, 50% probability ellipsoids).

has a chair conformation with the phosphonate substituents in equatorial positions. The fluorene groups are quite planar. The terminal methyl group of one ethoxy group is disordered over two conformations.

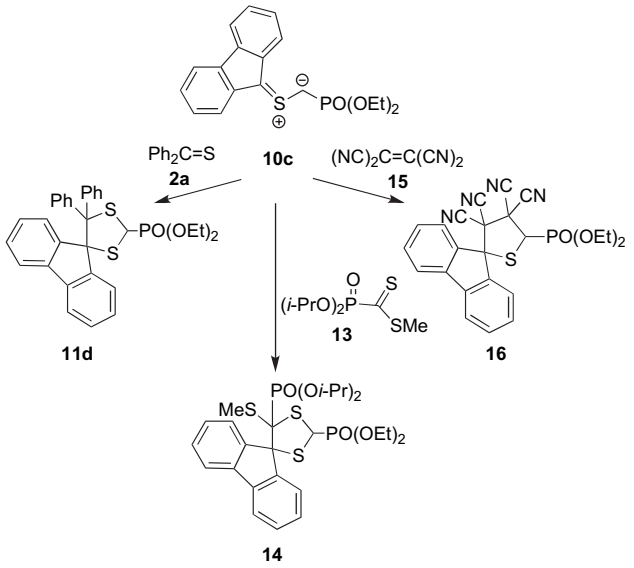


Scheme 3.

The experiment shows that the highly reactive **2b** already undergoes the [2+3] cycloaddition with **8a** at −65 °C to give regioselectively the 2,5-dihydro-1,3,4-thiadiazole **9c**, which is stable at this temperature. The decomposition starts only at ca. −45 °C, and thiocarbonyl ylide **10c** is formed as a transient species. In the absence of any intercepting agent, **10c** dimerizes regio- and stereoselectively to give **12** exclusively. Under these conditions, 1,3-dipolar electrocyclization to the corresponding thiirane is completely suppressed by the dimerization process. The mechanism of the head-to-head dimerization can be formulated in line with earlier results to occur via a 1,6-diradical.[14]

When **2b** was added to a freshly prepared solution of **9c** at −65 °C and the mixture was subsequently warmed to room temperature, typical workup by crystallization gave the 1,3-dithiolane-2-phosphonate **11c** in almost quantitative yield (Scheme 3). Similar to **11a**, in the ^{1}H NMR spectrum, H–C(2) appears at 5.52 ppm as a doublet ($^2J_{HP}$=6.6 Hz), and C(2) appears as a doublet at 43.6 ppm ($^1J_{CP}$=152.4 Hz). As no dimer **12** could be detected in the crude mixture (^{1}H NMR), thiocarbonyl ylide **10c** must have been trapped completely by the 'superdipolarophile' **2b**. A similar result was obtained with **2a** instead of **2b**. Also in this case, no dimerization was observed, and the structure of the mixed 1,3-dithiolane **11d** was attributed to the product isolated by crystallization (Scheme 4).

In addition to the thioketones **2a** and **2b**, *S*-methyl diisopropyl phosphonodithioformate (**13**) was tested as a C=S dipolarophile. Recently, it has been shown that **13** is an efficient interceptor of aromatic and cycloaliphatic thiocarbonyl *S*-methanides.[15] The reaction with **10c**, generated at −45 °C, led to the expected 1,3-dithiolane-2,4-diphosphonate **14**[16] (Scheme 4). Again, neither the corresponding thiirane nor

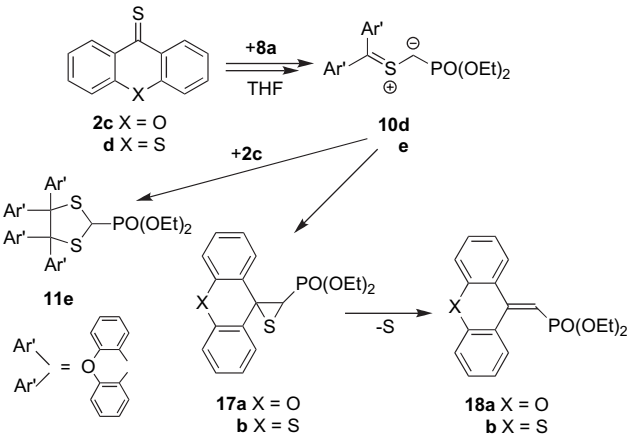


Scheme 4.

the dimer could be detected. Therefore it can be concluded that **13** is a superior dipolarophile, comparable with the frequently used **2a** and **2b**.

From the selected *C*,*C*-dipolarophiles, i.e., maleic anhydride, *N*-cyclohexylmaleimide, and tetracyanoethane, only the latter was able to trap **10c** to yield tetrahydrothiophene **16** (Scheme 4). No formation of any side-product was observed in this reaction.

It is well known that 9*H*-xanthene-9-thione (**2c**) and 9*H*-thioxanthene-9-thione (**2d**) belong to the moderately reactive aromatic thioketones.[12] With **8a** in THF, **2c** reacted slowly at room temperature with evolution of nitrogen. The mixture decolorized within 24 h and gave two products **11e** and **18a** in a ratio of 5:1 (Scheme 5). In the ^{1}H NMR spectrum, **11e** showed a doublet at 5.53 ppm ($^1J_{HP}$=6.1 Hz), whereas the corresponding signal of **18a** appeared at 5.92 ppm ($^1J_{HP}$=8.9 Hz). The same products were obtained when the reaction was carried out in boiling THF, but in this case, the ratio was determined as 2:3. Finally, after addition of **2c** to a boiling solution of **8a** in toluene, only the

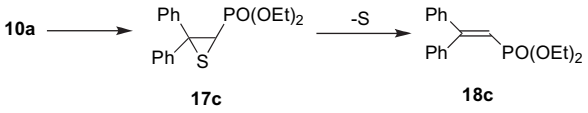


Scheme 5.

vinylphosphonate **18a** was formed. In this system, the intermediate **10d** undergoes an electrocyclic ring closure to give **17a** or enter a competitive [2+3] cycloaddition with the parent thioketone **2c**. Spontaneous desulfurization of **17a** leads to the isolated product **18a**. Consequently, higher dilution and increased temperature favor the formation of **18a**.

The less reactive **2d** reacted with **8a** only at enhanced temperature to give two products characterized as thiirane **17b** and vinylphosphonate **18b**, but no formation of a 1,3-dithiolane of type **11** was observed. Whereas the doublet for =CH– of **18b** was observed in the ^{1}H NMR spectrum in the typical region at ca. 6 ppm, the signal of the corresponding H–C(2) of **17b** was found at 2.74 ppm ($^1J_{HP}$=11.0 Hz). In boiling THF, the ratio of the two products was ca. 9:1 in favor of **17b**, whereas in boiling toluene, the proportion of **18b** increased (ratio 3:1). The separation of the products was achieved by chromatography.

Prompted by the results obtained with **2c** and **2d**, the reactions of **8a** with **2a** and **2b** (Scheme 2) were repeated in boiling toluene. In the case of **2a**, the corresponding vinylphosphonate **18c** was obtained as the sole product (Scheme 6). However, the reaction with **2b**, despite higher dilution, led to 1,3-dithiolane **11c** (Scheme 3) exclusively, which confirmed the outstanding dipolarophilicity of this thioketone.



Scheme 6.

3. Conclusion

In conclusion, the described results show that diazomethylphosphonates are attractive reagents for 1,3-dipolar cycloadditions, which in the case of C=S dipolarophiles exceed the reactivity of the frequently used diazoacetates. The presence of the phosphono group strongly influences the reactivity of the resulting thiocarbonyl ylides. The synthetic applications of these intermediates are limited by the availability of their precursors, and only 'thiofluorenone' **2b** is sufficiently reactive toward **8a** to give the appropriate 2,5-dihydro-1,3,4-thiadiazole derivative **9c**. The dominant tendency for cyclodimerization of **10c** can be suppressed only by addition of very reactive dipolarophiles to the reaction mixture.

4. Experimental

4.1. General

The ^{1}H and ^{13}C NMR spectra were recorded at ca. 21 °C with a Varian Gemini 200 BB VT (^{1}H at 200.1 MHz, ^{13}C at 50.3 MHz) or a Bruker-AC-300 (^{1}H at 300.1 MHz, ^{13}C at 75.5 MHz) spectrometer using $CDCl_3$ as a solvent. Chemical shifts (δ) are reported in parts per million downfield from internal TMS. The majority of signals were assigned with the aid of ATP or DEPT spectra. IR spectra were recorded in KBr pellets or as films on a Thermo-Nicolet Nexus FTIR spectrometer. Low- and high-resolution EI mass spectra (MS and HRMS) were taken on a Finnigan MAT 95 spectrometer at 70 eV. Melting points (uncorrected) were determined in capillary or on a Boëtius apparatus.

Column chromatography was carried out using silica gel (Merck 60, 0.063–0.200 μm). Thin layer chromatography (TLC) was performed on Merck 5554 aluminum-backed SiO_2 plates; products were visualized by UV light.

Toluene and THF were distilled from the blue solution of sodium benzophenone ketyl.

Thiobenzophenone (**2a**),[17] 9*H*-fluorene-9-thione (**2b**),[18] 9*H*-xanthene-9-thione (**2c**),[17] and 9*H*-thioxanthene-9-thione (**2d**)[17] were prepared following the literature procedure.

Methyl and ethyl diazomethylphosphonates (**8**) were prepared by the Seyferth method.[19]

4.2. Reaction of thiobenzophenone (2a) with diethyl and dimethyl diazomethylphosphonate (8a) and (8b)

To a solution of 1 mmol of thiobenzophenone (**2a**) in dry THF (1 mL) at −65 °C, 1 mmol of diazomethylphosphonate **8a** or **8b**, respectively, was added drop-wise. The mixture was stirred and allowed to warm to room temperature (decolorization of the mixture was observed at −15 °C). The solvent was evaporated and the solid residue was purified by recrystallization.

An analogous experiment was carried out at room temperature leading to the same result.

4.2.1. Diethyl (4,4,5,5-tetraphenyl-[1,3]dithiolan-2-yl)-phosphonate (11a). Yield: 200 mg (74%). Colorless solid. Mp 114–118 °C (decomp.; hexane/AcOEt). ^{1}H NMR: δ 1.41 (t, J=7.0 Hz, $2CH_3$), 4.16 (d, $^2J_{HP}$=6.6 Hz, CH), 4.20–4.34 (m, $2CH_2O$), 6.94–7.79 (m, 20arom. H). ^{13}C NMR: δ 16.4 (d, $^3J_{CP}$=5.9 Hz, $2CH_3$), 40.8 (d, $^1J_{CP}$=150.9 Hz, CHP), 63.6 (d, $^2J_{CP}$=6.7 Hz, $2CH_2O$), 79.6 (d, $^3J_{CP}$=7.0 Hz, $2C_q$), 126.1, 126.5, 126.6, 127.7, 127.9, 129.0, 131.1, 131.9 (20arom. CH), 142.4, 142.6 (4arom. C_q). IR (KBr, cm^{-1}): 3059m, 2981m, 1490s, 1443s, 1258s (P=O), 1043s and 1020s (P–O–C), 738m, 696s, 532m. ESI-MS m/z (%): 569 (100, $[M+Na]^+$). Anal. Calcd for $C_{31}H_{31}O_3PS_2$ (546.69): C 68.11, H 5.72; found: C 68.24, H 5.46.

4.2.2. Dimethyl (4,4,5,5-tetraphenyl-[1,3]dithiolan-2-yl)-phosphonate (11b). Yield: 250 mg (96%). Colorless solid. Mp 84–86 °C (decomp.; hexane/Et_2O). ^{1}H NMR: δ 3.90 (d, $^3J_{HP}$=11 Hz, $2CH_3O$), 4.20 (d, $^2J_{HP}$=6.9 Hz, CH), 6.80–7.70 (m, 20arom. H). ^{13}C NMR: δ 40.6 (d, $^1J_{CP}$=151.4 Hz, CHP), 54.3 (d, $^2J_{CP}$=6.7 Hz, $2CH_3O$), 79.9 (d, $^3J_{CP}$=7.3 Hz, $2C_q$), 126.7, 127.1, 127.3, 131.6, 132.3 (20arom. CH), 142.9 (4arom. C_q). IR (KBr, cm^{-1}): 3056m, 2953m, 1490s, 1443s, 1262s (P=O), 1054s and 1032s (P–O–C), 739m, 700s, 532m. EIMS m/z (%): 518 (<1, M^+), 288 (9), 211 (22), 210 (100), 198 (30), 197 (9), 178 (27), 165 (46), 121 (26).

4.3. Reaction of diethyl diazomethylphosphonate (8a) with 9*H*-fluorene-9-thione (2b)

To a solution of 1 mmol of 9*H*-fluorene-9-thione (**2b**) in dry THF (1 mL), 1 mmol of diethyl diazomethylphosphonate (**8a**) was added drop-wise at −65 °C. After 10 min stirring at −65 °C, decolorization of the mixture was observed. For the synthesis of **12**, the mixture was stirred and allowed to warm to room temperature. For the synthesis of **11c**, **11d**, **14**, and **16**, a respective dipolarophile **2a**, **2b**, **13** or **15** (1 mmol) was added. The mixture was stirred and allowed to warm to room temperature. The solvent was removed in vacuum and the solid residue purified by recrystallization.

4.3.1. Tetraethyl dispiro[9*H*-fluorene-9,2′-[1,4]dithiane-3′,9″-[9*H*]fluorene]-5′,6′-diphosphonate (12). Yield: 160 mg (46%). Colorless solid. Mp 230–235 °C (decomp.; hexane/dichloromethane). ^{1}H NMR: δ 1.36 (t, J=7.0 Hz, 2CH$_3$), 1.37 (t, J=7.0 Hz, 2CH$_3$), 4.16–4.36 (m, 4CH$_2$O), 4.84 (dd, $^2J_{HP}$=24.9 Hz, $^3J_{HP}$=12.6 Hz, 2CH), 6.16–6.19 (m, 2arom. H), 6.63–6.69 (m, 2arom. H), 7.01–7.64 (m, 10arom. H), 9.05–9.10 (m, 2arom. H). ^{13}C NMR: δ 16.1 (s, 4CH$_3$), 38.0 (d, $^1J_{CP}$=133.1 Hz, 2*C*HP), 57.0 (2C$_q$), 63.1 (d, $^2J_{CP}$=58.6 Hz, 4CH$_2$O), 119.1, 120.1, 125.1, 126.4, 126.7, 127.7, 128.4, 128.6 (16arom. CH), 139.8, 140.5, 142.2, 148.3 (8arom. C$_q$). IR (KBr, cm^{-1}): 2983m, 1630w, 1446m, 1249s (P═O), 1023vs (P–O–C), 976s, 742s, 553m. CIMS (NH$_3$) *m*/*z* (%): 693 (100, [M+1]$^+$), 329 (21), 318 (45), 197 (17). Anal. Calcd for $C_{36}H_{38}O_6P_2S_2$ (692.77): C 62.42, H 5.53, S 9.26; found: C 62.10, H 5.50, S 9.22.

4.3.2. Diethyl dispiro[9*H*-fluorene-9,4′-[1,3]dithiolan-5′,9″-[9*H*]fluorene]-2′-phosphonate (11c). Yield: 400 mg (74%). Colorless solid. Mp 242–252 °C (decomp.; hexane/dichloromethane). ^{1}H NMR: δ 1.41 (t, J=7.0 Hz, 2CH$_3$), 4.28–4.38 (m, 2CH$_2$O), 5.52 (d, $^2J_{HP}$=6.6 Hz, CH), 7.09–7.64 (m, 20arom. H). ^{13}C NMR: δ 16.4 (d, $^3J_{CP}$=5.8 Hz, 2CH$_3$), 43.6 (d, $^1J_{CP}$=152.4 Hz, CHP), 63.9 (d, $^2J_{CP}$=6.8 Hz, 2CH$_2$O), 75.0 (d, $^3J_{CP}$=7.0 Hz, 2C$_q$), 119.0, 119.5, 126.1, 126.7, 128.6, 128.7 (20arom. CH), 127.7, 140.1 (4arom. C$_q$). IR (KBr, cm^{-1}): 3055m, 2981m, 2905m, 1476m, 1446s, 1259vs (P═O), 1047vs and 1020vs (P–O–C), 964s, 741vs, 650m, 533m. CIMS (NH$_3$) *m*/*z* (%): 562 (15), 561 (37), 560 (100, [M+NH$_4$]$^+$), 543 (15), 349 (13), 348 (17), 329 (21), 202 (28), 200 (15), 197 (27). Anal. Calcd for $C_{31}H_{27}O_3PS_2$ (542.66): C 68.61, H 5.02, S 11.82; found: C 68.50, H 4.95, S 12.33.

4.3.3. Diethyl 5′,5′-diphenylspiro[9*H*-fluorene-9,4′-[1,3]dithiolane]-2-phosphonate (11d). Yield: 200 mg (37%). Colorless solid. Mp 172–178 °C (decomp.; hexane/Et$_2$O). ^{1}H NMR: δ 1.42 (t, J=7.0 Hz, 2CH$_3$), 4.29–4.38 (m, 2CH$_2$O), 5.01 (d, $^2J_{HP}$=6.7 Hz, CH), 5.65–5.67 (m, 1arom. H), 6.73–7.36 (m, 13arom. H), 7.73–7.80 (m, 4arom. H). ^{13}C NMR: δ 16.5 (d, $^3J_{CP}$=6.0 Hz, 2CH$_3$), 42.1 (d, $^1J_{CP}$=149.7 Hz, CHP), 63.8 (d, $^2J_{CP}$=6.9 Hz, CH$_2$O), 63.9 (d, $^2J_{CP}$=6.7 Hz, CH$_2$O), 75.9, 78.0 (2C$_q$), 120.1, 120.5, 124.7, 126.5, 126.7, 127.1, 127.5, 127.7, 128.1, 128.2, 129.0 (18arom. CH), 132.0, 138.3, 140.4, 142.8, 145.1, 148.0 (6arom. C$_q$). IR (KBr, cm^{-1}): 3055m, 2981m, 2905m, 1475m, 1444s, 1257s (P═O), 1046vs and 1020vs (P–O–C), 975s, 745vs, 699s, 536m. CIMS (NH$_3$) *m*/*z* (%): 563 (37, [M+NH$_4$]$^+$), 562 (100), 546 (8, [M+1]$^+$), 545 (21, M$^+$), 366 (38), 349 (20), 317 (45), 210 (18), 200 (16), 199 (78), 197 (33). Anal. Calcd for $C_{31}H_{29}O_3PS_2$ (544.68): C 68.36, H 5.37, S 11.77; found: C 67.88, H 5.30, S 12.22.

4.3.4. Diisopropyl [2-(diethoxyphosphoryl)-5-methylsulfanylspiro[9*H*-fluorene-9,4′-[1,3]dithiolane]-5-phosphonate (14). Yield: 260 mg (43%). Colorless solid. Mp 160–170 °C (decomp.; hexane/dichloromethane). ^{1}H NMR: δ 0.74 (d, J=6.2 Hz, CH$_3$), 0.93 (d, J=6.2 Hz, CH$_3$), 1.16 (d, J=6.1 Hz, CH$_3$), 1.30 (d, J=6.1 Hz, CH$_3$), 1.59 (t, J=6.9 Hz, CH$_3$), 1.60 (t, J=6.9 Hz, CH$_3$), 2.73 (s, CH$_3$S), 4.43–4.68 (m, 2CH$_2$O, 2CHO), 5.40 (dd, $^2J_{HP}$=4.6, $^4J_{HP}$=1.1 Hz, CH), 7.36–7.79 (m, 6arom. H), 8.34–8.37 (m, 1arom. H), 8.68–871 (m, 1arom. H). ^{13}C NMR: δ 16.3 (d, $^3J_{CP}$=7.2 Hz, *C*H$_3$CH$_2$O), 16.5 (d, $^3J_{CP}$=14.0 Hz, *C*H$_3$CH$_2$O), 22.0 (d, $^3J_{CP}$=6.4 Hz, CH$_3$S), 23.0, 23.5, 23.6, 23.9 (2(*C*H$_3$)$_2$CH), 42.7 (dd, $^1J_{CP}$=150.0, $^3J_{CP}$=11.0 Hz, CHP), 63.6 (d, $^2J_{CP}$=6.9 Hz, CH$_2$O), 64.4 (d, $^2J_{CP}$=6.6 Hz, CH$_2$O), 71.0 (d, $^2J_{CP}$=8.3 Hz, (CH$_3$)$_2$*C*H), 73.3 (d, $^2J_{CP}$=7.9 Hz, (CH$_3$)$_2$*C*H), (2C$_q$ not found), 118.4, 119.3, 125.9, 126.6, 128.5, 129.1, 129.2, 130.7 (8arom. CH), 139.2, 140.3, 142.6, 149.4 (4arom. C$_q$). IR (KBr, cm^{-1}): 3058w, 2979m, 2925w, 1448m, 1386m, 1256s, 1244s (P═O), 1046s, 1010vs and 985vs (P–O–C), 743vs, 534m. CIMS (NH$_3$) *m*/*z* (%): 604 (32, [M+1]$^+$), 603 (100, M$^+$), 389 (28), 375 (11), 202 (12), 200 (16).

4.3.5. Diethyl 3,3,4,4-tetracyano-spiro[9*H*-fluorene-9,2′-thiolane]-5-phosphonate (16). Yield: 240 mg (51%). Pale-yellow solid. Mp 159–162 °C (decomp.; Et$_2$O). ^{1}H NMR: δ 1.40–1.47 (m, 2CH$_3$), 4.31–4.44 (m, 2CH$_2$O), 4.70 (d, $^2J_{HP}$=16.3 Hz, CH), 7.18–7.77 (m, 7arom. H), 8.15–8.17 (m, 1arom. H). ^{13}C NMR: δ 16.2 (d, $^3J_{CP}$=5.1 Hz, CH$_3$), 16.2 (d, $^3J_{CP}$=4.6 Hz, CH$_3$), 49.5 (d, $^1J_{CP}$=147.3 Hz, CHP), 52.1, 60.0 (2C$_q$), 65.4 (d, $^2J_{CP}$=6.9 Hz, CH$_2$O), 65.8 (d, $^2J_{CP}$=6.9 Hz, CH$_2$O), 107.5, 109.2, 109.4, 109.5 (4CN), 120.7, 120.8, 126.6, 128.2, 128.3, 128.7, 131.5, 131.8 (8arom. C), 139.8, 141.2, 142.7 (4arom. C$_q$). IR (KBr, cm^{-1}): 3064w, 2987m, 2920m, 2255w, 1451m, 1264s (P═O), 1043vs and 1017vs (P–O–C), 752s, 744s, 548m. CIMS (NH$_3$) *m*/*z* (%): 492 (100, [M+NH$_4$]$^+$), 292 (40), 264 (27). Anal. Calcd for $C_{31}H_{19}N_4O_3PS_2$ (474.48): C 60.75, H 4.04, N 11.85, S 6.76; found: C 60.55, H 4.04, N 11.64, S 6.61.

4.4. Reaction of diethyl diazomethylphosphonate (8a) with 9*H*-xanthene-9-thione (2c) and 9*H*-thioxanthene-9-thione (2d)

To a solution of 1 mmol of 9*H*-xanthene-9-thione (**2c**) in dry THF (1 mL), 1 mmol of diethyl diazomethylphosphonate (**8a**) was added drop-wise at room temperature. After 24 h stirring, decolorization of the mixture was observed. The solvent was removed under vacuum and compound **11e** was separated and purified by recrystallization. The same reaction in boiling THF gave products **11e** and **18a** in a 2:3 ratio, whereas in boiling toluene the formation of only **18a** was observed. The reaction with **2d** was carried out in boiling toluene. Two products were separated chromatographically on silica gel (hexane/AcOEt).

4.4.1. Diethyl dispiro[9*H*-xanthene-9,4′-[1,3]dithiolane-5′,9″-[9*H*]xanthene]-2′-phosphonate (11e). Yield: 180 mg (63%). Colorless solid. Mp 156–158 °C (decomp.; hexane/dichloromethane). ^{1}H NMR: δ 1.48 (t, J=7.0 Hz, 2CH$_3$), 4.37–4.47 (m, 2CH$_2$O), 5.53 (d, $^2J_{HP}$=6.1 Hz, CH), 6.67–7.52 (m, 14arom. H), 8.04–8.07 (m, 2arom. H). ^{13}C NMR: δ 16.5 (d, $^3J_{CP}$=5.8 Hz, 2CH$_3$), 43.9 (d, $^1J_{CP}$=153.3 Hz, CHP), 63.9 (d, $^2J_{CP}$=6.9 Hz, 2CH$_2$O), 74.5 (d, $^3J_{CP}$=7.1 Hz, 2C$_q$), 115.5, 116.0, 121.9, 128.7, 128.9, 130.3 (16arom. CH), 151.3, 151.8 (4arom. C$_q$). IR (KBr, cm^{-1}): 2983w, 2915w, 1597m, 1474s, 1443s, 1308m, 1281m, 1246s (P═O), 1044s and 1017vs (P–O–C), 749s, 536m. ESI-MS m/z (%): 597 ([M+Na]$^+$). Anal. Calcd for $C_{31}H_{27}O_5PS_2$ (574.65): C 64.53, H 4.68, S 10.95; found: C 64.79, H 4.74, S 11.16.

4.4.2. Diethyl (9*H*-xanthen-9-ylidene)methylphosphonate (18a). Yield: 200 mg (61%). Colorless solid. Mp 72–73 °C (hexane). ^{1}H NMR: δ 1.22 (t, J=7.0 Hz, 2CH$_3$), 3.98–4.12 (m, 2CH$_2$O), 5.92 (d, $^2J_{HP}$=8.9 Hz, CH), 7.16–7.28 (m, 4arom. H), 7.38–7.47 (m, 2arom. H), 7.71–7.74 (m, 1arom. H), 8.52–8.55 (m, 1arom. H). ^{13}C NMR: δ 16.2 (d, $^3J_{CP}$=6.6 Hz, 2CH$_3$), 61.8 (d, $^2J_{CP}$=6.0 Hz, 2CH$_2$O), 105.3 (d, $^1J_{CP}$=198.2 Hz, CHP), 116.6, 117.2 (2arom. C), 119.8 (d, $^2J_{CP}$=7.1 Hz, C$_q$), 123.2, 124.1, 124.2, 129.6, 130.8, 131.5 (8arom. CH), 143.8, 143.9, 151.3, 152.0 (4arom. C$_q$). IR (KBr, cm^{-1}): 3058w, 3033w, 2985m, 2900w, 1604s, 1564m, 1477m, 1456s, 1391w, 1361w, 1320m, 1284m, 1245s 1236s (P═O), 1047s and 1035s (P–O–C), 966s, 788s, 770s, 547m. CIMS (NH$_3$) m/z (%): 348 (7, [M+NH$_4$]$^+$), 333 (8), 332 (20), 331 (100, [M+1]$^+$). Anal. Calcd for $C_{18}H_{19}O_4P$ (330.32): C 65.45, H 5.80; found: C 65.30, H 5.92.

4.4.3. Spiro[thiirane-2,9′-[9*H*]thioxanthene]-3-phosphonate (17b). Yield: 190 mg (50%). Eluted with hexane/AcOEt 1:1 and recrystallized from hexane. Pale-yellow solid. Mp 69–72 °C (hexane). ^{1}H NMR: δ 1.16 (t, J=7.1 Hz, CH$_3$), 1.18 (t, J=7.1 Hz, CH$_3$), 2.74 (d, $^2J_{HP}$=11.0 Hz, CH), 3.76–3.92 (m, 2CH$_2$O), 7.19–7.28 (m, 4arom. H), 7.45–7.49 (m, 2arom. H), 7.60–7.63 (m, 1arom. H), 7.68–7.71 (m, 1arom. H). ^{13}C NMR: δ 16.3 (d, $^3J_{CP}$=4.2 Hz, 2CH$_3$), 40.7 (d, $^1J_{CP}$=184.1 Hz, CHP), 55.1 (C$_q$), 62.4 (d, $^2J_{CP}$=6.5 Hz, CH$_2$O), 63.0 (d, $^2J_{CP}$=6.7 Hz, CH$_2$O), 126.1, 126.2, 126.6, 126.8, 127.5, 127.7, 130.3 (8arom. CH), 133.0, 136.1, 136.4, 137.0 (4arom. C$_q$). IR (KBr, cm^{-1}): 3057w, 2982m, 2929w, 2904w, 1457m, 1441m, 1263s, 1243m (P═O), 1045s and 1027s (P–O–C), 971s, 787m, 742s, 545m. CIMS (NH$_3$) m/z (%): 380 (5), 379 (10), 378 (44, M$^+$), 365 (10), 363 (46), 347 (21), 346 (100, [M−S]$^+$), 332 (20), 331 (13). Anal. Calcd for $C_{18}H_{19}O_3PS_2$ (378.45): C 57.13, H 5.06, S 16.94; found: C 57.16, H 4.99, S 16.83.

4.4.4. Diethyl (9*H*-thioxanthen-9-ylidene)methylphosphonate (18b). Yield: 100 mg (29%). Eluted with AcOEt and recrystallized from hexane. Colorless solid. Mp 74–75 °C (hexane). ^{1}H NMR: δ 1.11 (t, J=7.1 Hz, CH$_3$), 1.12 (t, J=7.1 Hz, CH$_3$), 3.86–3.97 (m, 2CH$_2$O), 5.92 (d, $^2J_{HP}$=12.5 Hz, CH), 7.26–7.36 (m, 4arom. H), 7.43–7.49 (m, 2arom. H), 7.63–7.66 (m, 1arom. H), 8.19–8.22 (m, 1arom. H). ^{13}C NMR: δ 16.0 (d, $^3J_{CP}$=6.8 Hz, 2CH$_3$), 61.8 (d, $^2J_{CP}$=6.1 Hz, 2CH$_2$O), 115.4 (d, $^1J_{CP}$=191.6 Hz, CHP), 125.8, 125.9, 126.1, 126.3, 127.1, 128.4, 128.9, 130.2 (8arom. CH), 131.9 (d, $^2J_{CP}$=5.6 Hz, C$_q$), 136.0, 136.3, 151.9, 152.0 (4arom. C$_q$). IR (KBr, cm^{-1}): 3053w, 2980w, 2934w, 2903w, 1586m, 1559w, 1464w, 1438m, 1241s (P═O), 1160w, 1049s and 1035s (P–O–C), 960s, 934w, 843m, 778m, 764m, 548m. CIMS (NH$_3$) m/z (%): 364 (10, [M+NH$_4$]$^+$), 363 (46), 348 (13), 347 (21), 346 (100, M$^+$). Anal. Calcd for $C_{18}H_{19}O_3PS$ (346.39): C 62.42, H 5.53, S 9.26; found: C 62.35, H 5.38, S 9.32.

4.5. X-ray crystal-structure determination of 11a and 12

All measurements were performed on a Nonius KappaCCD area-diffractometer[20] using graphite-monochromated Mo Kα radiation (λ 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. The data collection and refinement parameters are given below[21] and views of the molecules are shown in Figures 1 and 2. Data reduction was performed with HKL Denzo and Scalepack.[22] The intensities were corrected for Lorentz and polarization effects, and absorption corrections based on the multi-scan method[23] were applied. Equivalent reflections were merged. The structures were solved by direct methods using SIR92[24] in the case of **11a** and SHELXS97[25] in the case of **12**, which revealed the positions of all non-H-atoms. In the case of **11a**, one ethyl group is disordered over two conformations. Two sets of overlapping positions were defined for the atoms of the disordered ethyl group and the site occupation factor of the major conformation of the group refined to 0.818(6). In the case of **12**, the terminal methyl group of one ethoxy moiety is disordered over two conformations. Two positions were defined for the atoms of the disordered methyl group and the site occupation factor of the major conformation refined to 0.51(3). For both structures, similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered C-atoms, while neighboring atoms within and between each conformation of the disordered ethyl groups were restrained to have similar atomic displacement parameters. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} of its parent C-atom (1.5U_{eq} for the methyl groups). The refinement of the structures was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the case of **12**. In **11a** and **12**, three and one reflections, respectively, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Neutral atom scattering factors for non-H-atoms were taken from Ref. 26, and the scattering factors for H-atoms were taken from Ref. 27. Anomalous dispersion effects were included in F_c;[28] the values for f' and f'' were those of Ref. 29. The values of the mass attenuation coefficients are those of Ref. 30. All calculations were performed using the SHELXL97[31] program.

Crystal data for **11a**: $C_{31}H_{31}O_3PS_2$, M=546.68, colorless, prism, crystal dimensions 0.15×0.25×0.32 mm, triclinic, space group $P\bar{1}$, Z=2, reflections for cell determination 32 546, 2θ range for cell determination 4–50°, a=8.4060(3) Å, b=9.8163(4) Å, c=17.4649(7) Å, α=87.447(3)°, β=76.876(2)°, γ=77.811(2)°, V=1371.84(9) Å^3,

T=160 K, D_X=1.323 g cm^{-3}, μ(Mo Kα)=0.284 mm^{-1}, scan type ω, $2\theta_{(max)}$=50°, transmission factors (min; max) 0.757; 0.966, total reflections measured 17 711, symmetry independent reflections 4832, reflections with $I>2\sigma(I)$ 3935, reflections used in refinement 4829, parameters refined 356; restraints 38, $R(F)$ [$I>2\sigma(I)$ reflections]=0.0407, $wR(F^2)$ [all data]=0.1055 ($w=[\sigma^2(F_o^2)+(0.0471P)^2+0.7354P]^{-1}$, where $P=(F_o^2+2F_c^2)/3$), goodness of fit 1.064, final Δ_{max}/σ=0.002, $\Delta\rho$ (max; min)=0.34; −0.50 e Å^{-3}.

Crystal data for **12**: $C_{36}H_{38}O_6P_2S_2$, M=692.76, colorless, prism, crystal dimensions 0.10×0.22×0.22 mm, monoclinic, space group $P2_1/n$, Z=4, reflections for cell determination 63 677, 2θ range for cell determination 4–60°, a=12.1758(1) Å, b=13.0645(1) Å, c=21.1455(2) Å, β=93.5396(7)°, V=3357.21(5) Å^3, T=160 K, D_X=1.370 g cm^{-3}, μ(Mo Kα)=0.300 mm^{-1}, scan type ϕ and ω, $2\theta_{(max)}$=60°, transmission factors (min; max) 0.868; 0.973, total reflections measured 89 162, symmetry independent reflections 9809, reflections with $I>2\sigma(I)$ 7639, reflections used in refinement 9808, parameters refined 431; restraints 7, $R(F)$ [$I>2\sigma(I)$ reflections]=0.0443, $wR(F^2)$ [all data]=0.1198 ($w=[\sigma^2(F_o^2)+(0.0536P)^2+1.7904P]^{-1}$, where $P=(F_o^2+2F_c^2)/3$), goodness of fit 1.062, secondary extinction coefficient 0.0021(6), final Δ_{max}/σ=0.001, $\Delta\rho$ (max; min)=0.36; −0.53 e Å^{-3}.

Acknowledgements

This project was supported by the grant No. 505/681/2004 from the University of Łódź. We acknowledge the financial support by the Polish State Committee for Scientific Research (Grant No. 4 T09A 046 25) and F. Hoffmann-La Roche AG, Basel.

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