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FORMATION OF PHOSPHONYLATED THIIRANES IN THE REACTION OF A DIAZOMETHANEPHOS- PHONATE AND CYCLOALIPHATIC THIOKETONES

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Dedicated to Professor Yoshito Kishi at the occasion of his 70th birthday

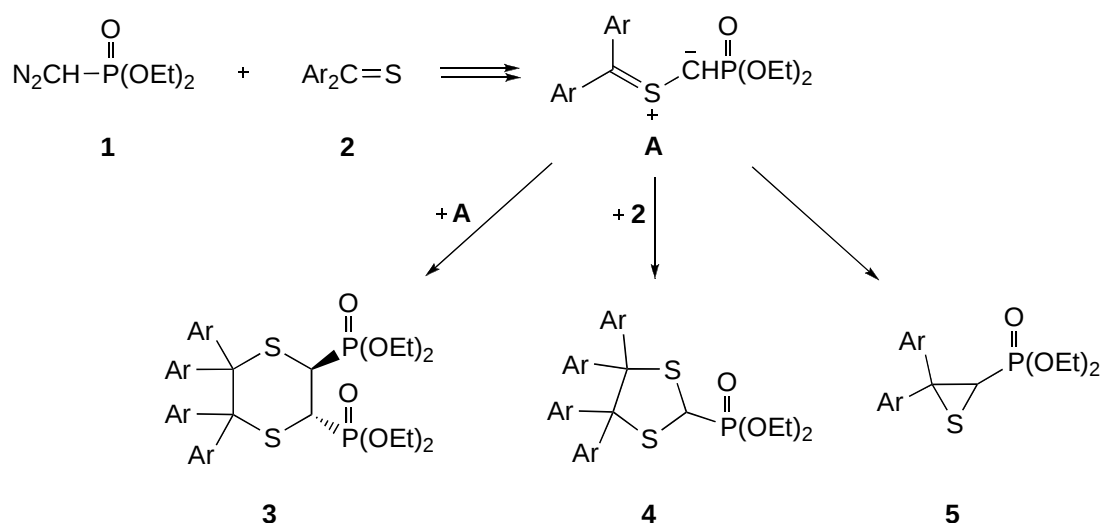
Abstract – The reaction of diethyl diazomethanephosphonate (**1**) with cycloaliphatic thioketones (**6**) in THF at room temperature leads to the corresponding thiirane-2-phosphonates (**7**) in good yield. A reaction mechanism via 1,3-dipolar cycloaddition of the diazo compound with the C=S group to give the 2,5-dihydro-1,3,4-thiadiazole-2-phosphonate as an intermediate, which spontaneously eliminates nitrogen is most likely. The resulting thiocarbonyl ylide undergoes a 1,3-dipolar electrocyclization to yield a thiirane. These products can be desulfurized smoothly by treatment with tris(diethylamino)phosphine to give α,β -unsaturated phosphonates.

INTRODUCTION

In a recent paper we described the reaction of diethyl diazomethanephosphonate (**1**) with aromatic thioketones (**2**).¹ The most reactive thioketones, i.e., 9*H*-fluorene-9-thione and thiobenzophenone, in THF reacted with **1** at temperatures below 0 °C to give 1,4-dithianes (**3**) and 1,3-dithiolanes (**4**), respectively (*Scheme 1*). On the other hand, the less reactive 9*H*-xanthene-9-thione and **1** in refluxing toluene yielded the corresponding thiirane (**5**) together with the phosphonylated ethylene as the product of a spontaneous

desulfurization. The formation of all these products can be explained by subsequent reactions of in situ generated thiocarbonyl ylides of type **A**. These sulfur-containing 1,3-dipoles have been studied extensively in recent time.^{2,3} It is well established that the reaction of thiocarbonyl compounds with diazo compounds offers a very efficient access to these reactive intermediates, which are attractive building blocks for the preparation of diverse thiaheterocycles.⁴ The use of phosphonylated diazomethanes opens a convenient route to phosphonylated products in a one-pot reaction.

Scheme 1



Thiiranes are useful three-membered heterocycles which can be applied in the synthesis of more complex systems.⁵ Furthermore, some thiiranes found application as pharmaceuticals, agrochemicals or materials with special properties.⁶ It is also well known that the phosphonyl group is an important unit in organic compounds with respect to their biological activities and physicochemical properties.⁷ For this reason, hitherto very little known phosphonylated thiiranes of type (**5**) attracted our interest. The earlier studies (see ref.³) showed that aliphatic thiocarbonyl ylides prefer to undergo a 1,3-dipolar electrocyclization to give thiiranes instead of dimerization to **3** and 1,3-dipolar cycloadditions to yield **4**.

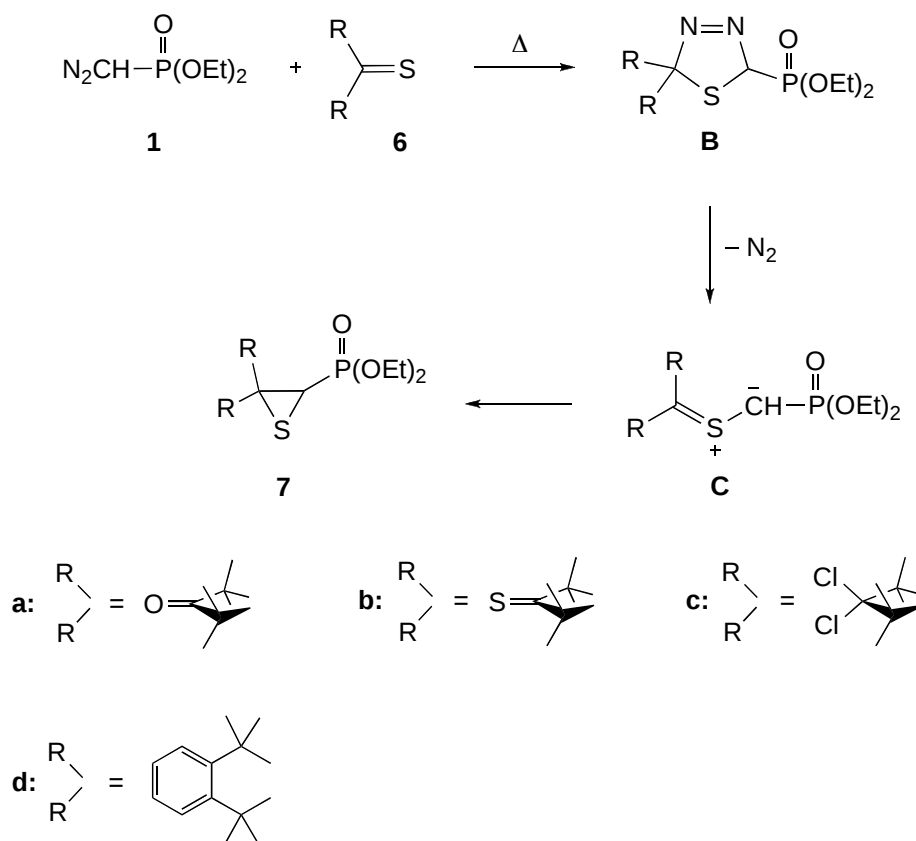
The aim of the present work was to examine the behavior of **1** in reactions with a series of cycloaliphatic thioketones (**6**) and to compare the reactivity of **1** with that of ethyl diazoacetate, which was the subject of an earlier study.⁸

RESULTS AND DISCUSSION

The sterically crowded 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**6a**)⁹ and the corresponding dithione (**6b**)¹⁰ are favorite model compounds for studies on the reactivity of the C=S function. Recently, we described the synthesis of 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (**6c**) as a new example of a

stable and synthetically useful thioketone.^{11,12} Typically, equimolar amounts of **1** and **6** in THF solution were heated to reflux whereby evolution of N₂ was observed. After 1–5 h, the red color of **6** vanished indicating the completion of the reaction. The ¹H-NMR spectrum of the crude mixtures showed in each case the formation of only one product in almost quantitative yield, which are characterized by a doublet at ca. 2.70–3.05 ppm with ²J_{H,P} ≈ 9.4 Hz. Pure products were obtained in moderate yields after crystallization from hexane. Attempted chromatographic workup led to decomposition of the products. The crystalline compounds were identified as thiiranes (**7a–c**) on the basis of their spectroscopic and analytical data (Scheme 2). In the reaction of **1** with 1,1,3,3-tetramethylindane-2-thione (**6d**) in THF under reflux, the expected thiirane (**7d**) was obtained as the sole product.

Scheme 2

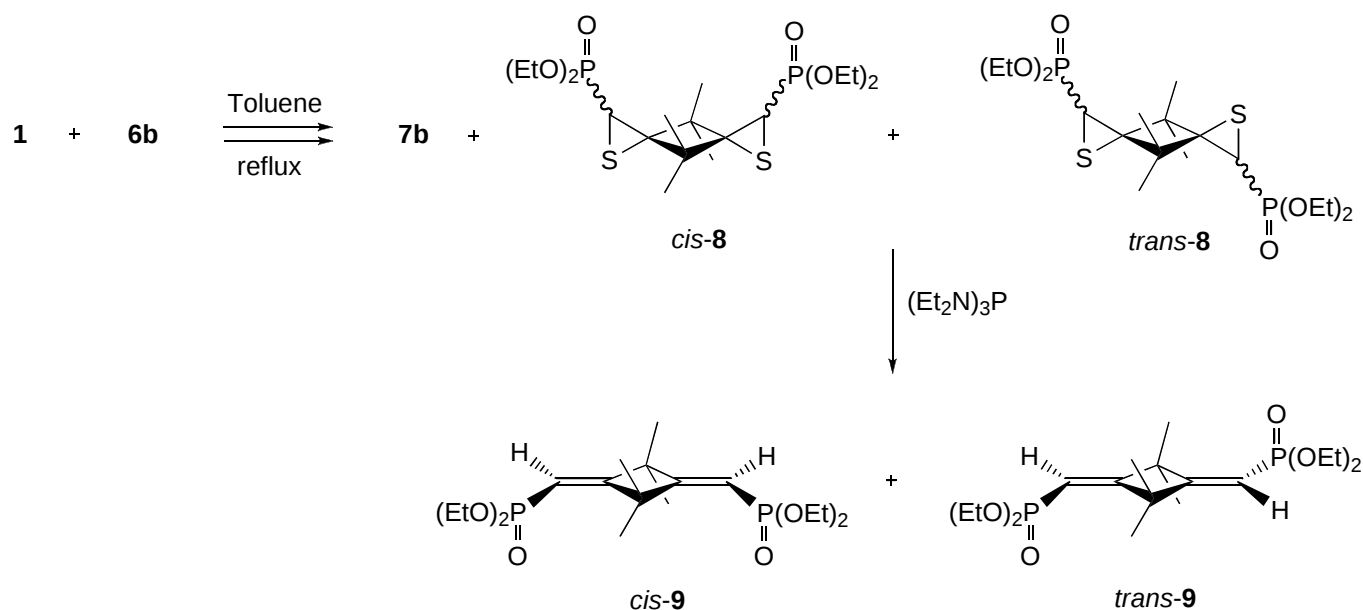


In order to test the thermal stability of the thiiranes (**7**), the reaction of **1** with **6a** was carried out in refluxing toluene. After addition of **6a**, the decolorization occurred immediately. According to the ¹H-NMR spectrum, **7a** was formed quantitatively, and no desulfurized product could be detected.

The analogous reaction of equimolar amounts of **1** and **6b** in refluxing toluene gave a mixture of **7b** and the stereoisomeric 2:1 products (*cis*-**8**) and (*trans*-**8**) (Scheme 3). When **1** was used in a three-fold excess, the mixture contained only bithiiranes **8** as a mixture of four diastereoisomers, which could be separated

neither by fractional crystallization nor by column chromatography. Desulfurization of the mixture obtained after attempted crystallization from hexane yielded the two bis-phosphonates *cis*-**9** and *trans*-**9** in a ratio of 1:4 (^1H -NMR). After crystallization and subsequent separation by preparative layer chromatography, the *trans*-isomer was obtained in pure form, which showed only one signal for 4 Me groups at 1.49 and 25.9 ppm, respectively.¹³

Scheme 3

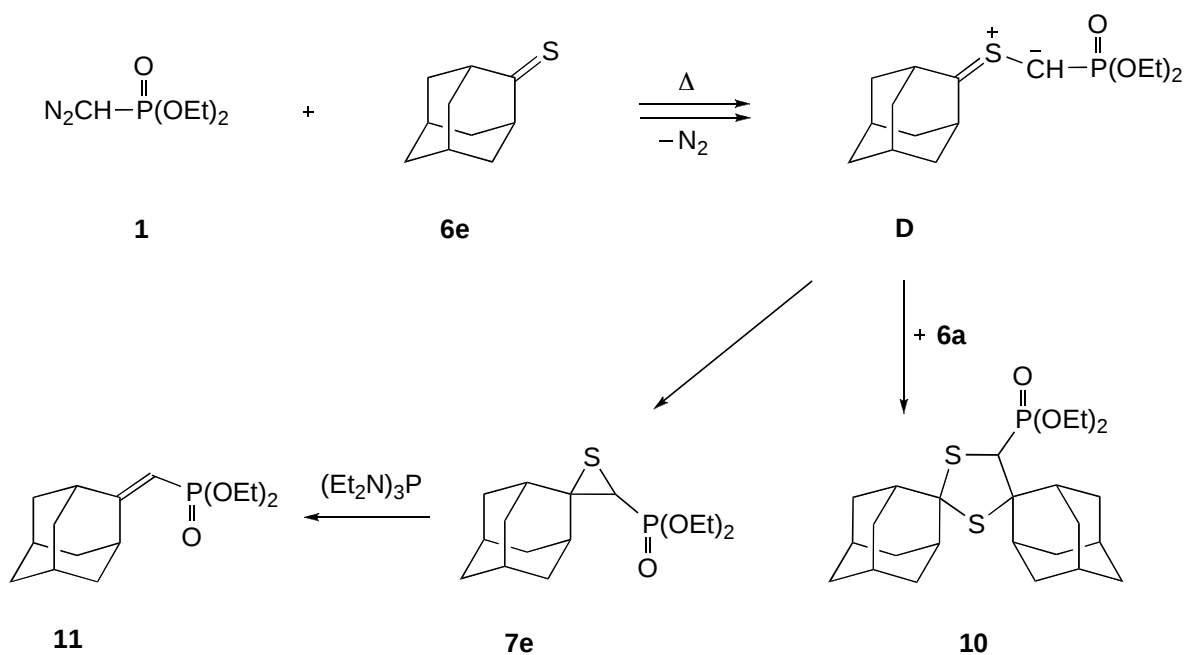


Whereas the reaction of **1** with adamantanethione (**6e**) in boiling toluene afforded the phosphonylated thiirane (**7e**) exclusively, heating of a mixture of **1** and **6e** in THF led to **7e** along with a second product, which in the ^1H -NMR spectrum showed a doublet located at 2.9 ppm ($^2J_{\text{H,P}} \approx 15.2$ Hz). After decolorization of the reaction mixture, the ^1H -NMR spectrum evidenced the presence of substantial amounts of **1**, which only after addition of another 0.5 equivalents of **6e** was completely consumed. In analogy to the thiiranes (**7a–d**), the doublet at 2.65 ppm ($^2J_{\text{H,P}} \approx 9.6$ Hz) can be attributed to **7e**. For the second product, the structure of 1,3-dithiolane (**10**) is likely, similar to the result of the reaction of **6e** with ethyl diazoacetate.⁸ All attempts to separate **7e** and **10** by chromatography (SiO_2) or crystallization were unsuccessful. For this reason, the crude reaction mixture, which was obtained in boiling toluene, was desulfurized by heating it with $(\text{Et}_2\text{N})_3\text{P}$ in THF solution. After chromatographic workup, (adamantylidene)methanephosphonate (**11**, Scheme 4) was isolated as a viscous oil in 56% yield.

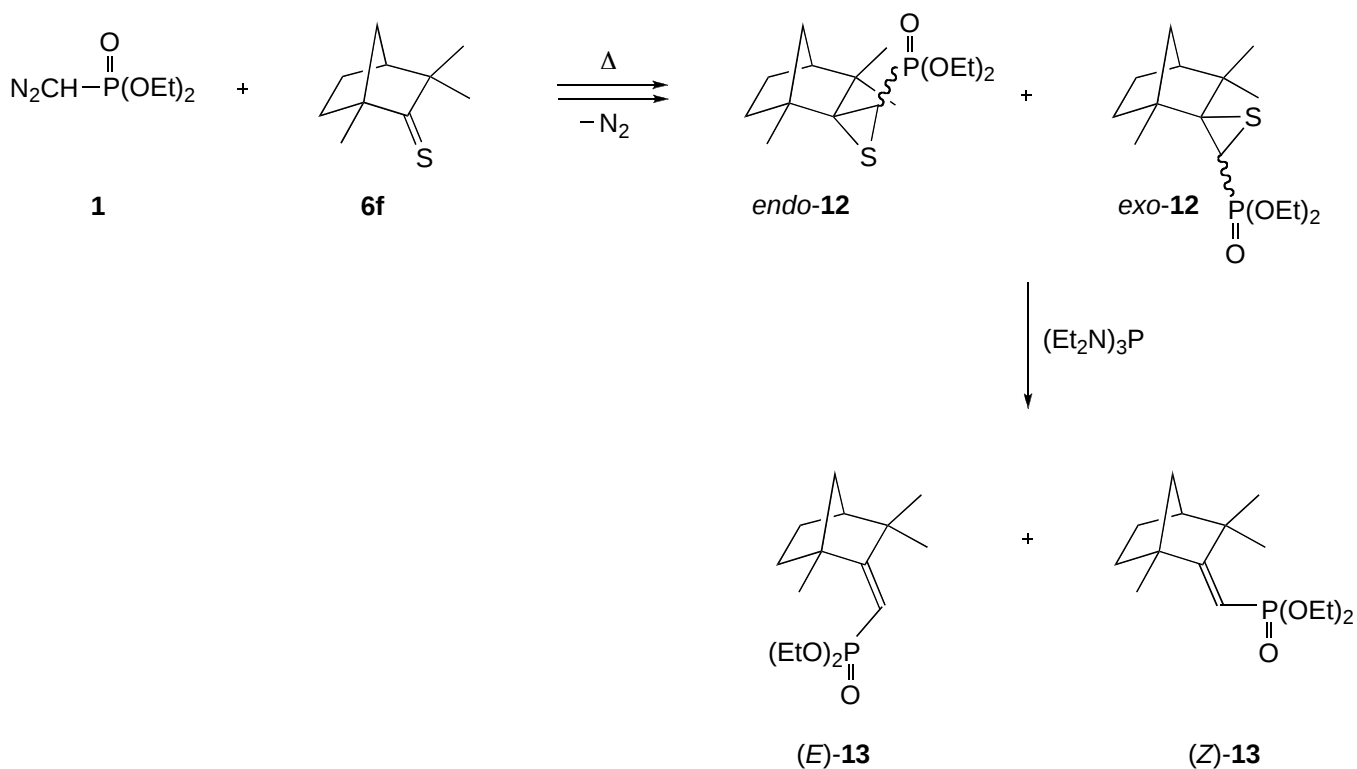
For the reaction of **1** with thiofenchone (**6f**), four stereoisomeric thiiranes can be expected.¹⁴ However, the experiment carried out in refluxing toluene gave only two products, which were identified by ^1H -NMR spectroscopy as thiiranes of type (**12**), based on the presence of two doublets at 2.75 and 2.80 ppm with $^2J_{\text{H,P}} \approx 4.8$ Hz and 3.6 Hz, respectively. The ratio of the products was estimated to *ca.* 3:1.¹⁶ Similar

to the examples shown in *Scheme 3* and *4*, desulfurization occurred smoothly by treatment with $(\text{Et}_2\text{N})_3\text{P}$, leading to a mixture of (*E*)- and (*Z*)-**13**, in which the ratio of the components is preserved (*Scheme 5*). After column chromatography (SiO_2), the major isomer was isolated in pure form.

Scheme 4

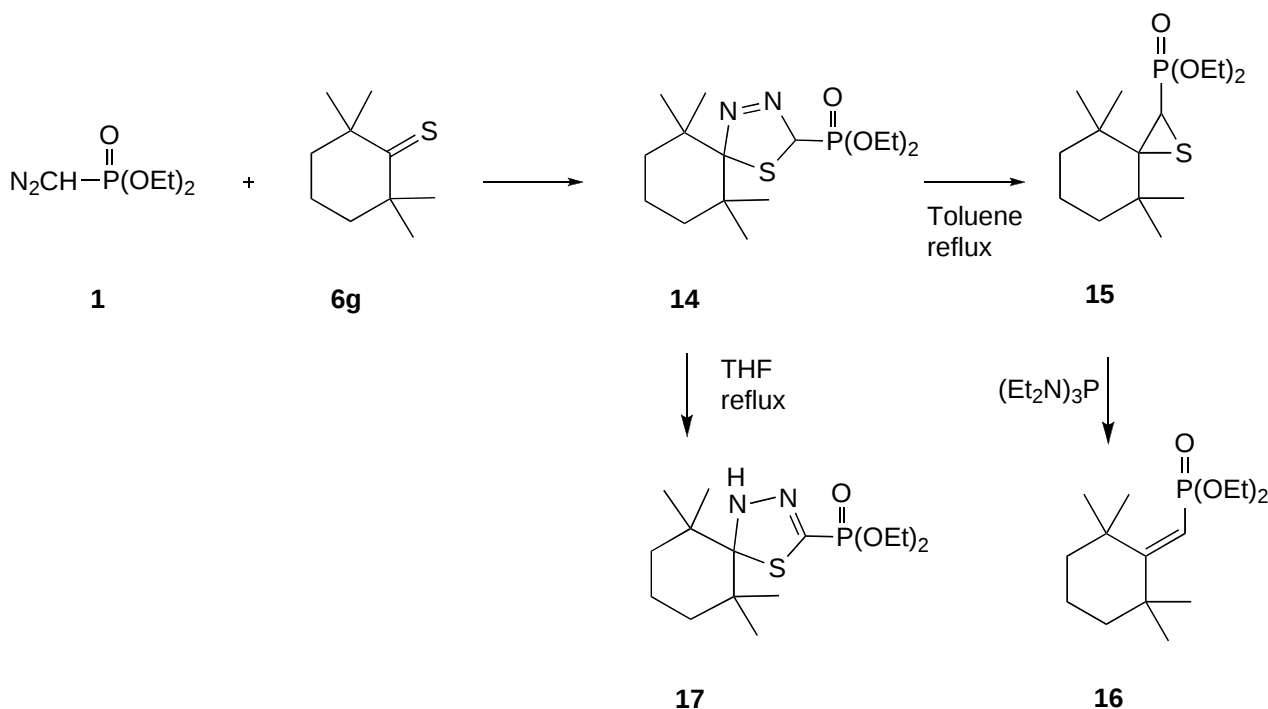


Scheme 5



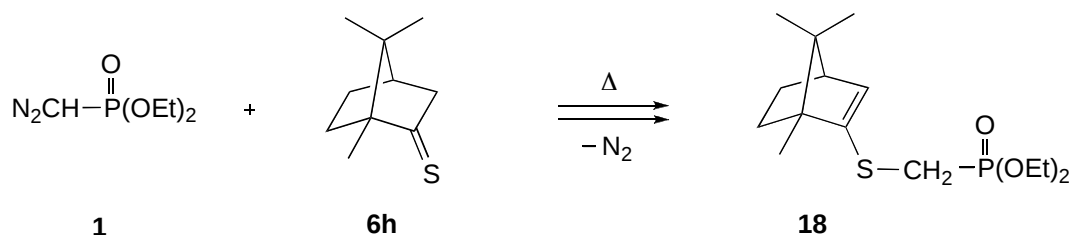
The sterically crowded 2,2,6,6-tetramethylcyclohexanethione (**6g**) reacted with **1** in boiling toluene to give thiirane (**15**), which without isolation was desulfurized by treatment with $(\text{Et}_2\text{N})_3\text{P}$ to give the expected α,β -unsaturated phosphonate (**16**) in 53% yield (*Scheme 6*). However, in a single experiment, which was carried out in refluxing THF solution, no evolution of N_2 was observed, indicating that no thiocarbonyl ylide is formed. In contrast to other products of the reactions of **1** and **6a–f**, the ^1H -NMR spectrum of the crystalline material obtained from **1** and **6g** in this experiment did not reveal any signal around 2.5 ppm, which is characteristic for CH of thiiranes of type **7**. Instead, a broad signal appeared at 6.60 ppm. In the IR spectrum (KBr), an absorption at 3250 cm^{-1} indicated the presence of an NH group. The MS spectrum and the elemental analyses confirmed the molecular formula of 1:1 adduct of **1** and **6g**. Based on these data and in analogy to a previously described compound,¹⁷ the structure of the 2,3-dihydro-1,3,4-thiadiazole (**17**) was attributed to this product (*Scheme 7*). A fast tautomerization of the initially formed **14** offers a plausible explanation for the formation of **17**.¹⁸

Scheme 6



Thiocamphor (**6h**) is known to undergo easily [2+3]-cycloadditions with diazomethane below $0\text{ }^\circ\text{C}$.¹⁵ Subsequent elimination of N_2 at $10\text{ }^\circ\text{C}$ leads to 2-methylsulfanyl-2-bornene, which is an isomer of the intermediate thiocarbonyl *S*-methanide. The formation of this product is explained by a 1,4-H-shift in the ylide (see also ref.²⁰). In the present study, heating of a mixture of **1** and **6h** in THF yielded again only one product (^1H -NMR) with two doublets at 2.94 ($^2J_{\text{H,P}} \approx 16.0\text{ Hz}$) and 5.58 ppm ($^3J_{\text{H,H}} \approx 4.3\text{ Hz}$). These data are in accordance with structure (**18**, *Scheme 7*), which is formed *via* an analogous 1,4-H-shift.

Scheme 7



In conclusion, reactions with aliphatic thioketones extend the synthetic applications of diazomethane phosphonates and open a straightforward access to phosphonylated thiiranes (**7**). These products can be desulfurized smoothly to give α,β -unsaturated phosphonates. From the mechanistic point of view, the reactions proceed *via* a regioselective [2+3]-cycloaddition, followed by N_2 elimination leading to reactive thiocarbonyl ylides, which, on turn, undergo a 1,3-dipolar electrocycloaddition. In contrast, the more reactive aromatic thioketones and **1** form phosphonylated thiocarbonyl ylides, which preferably dimerize or capture the starting thioketone to give 1,3-dithiolanes (*Schönberg* products).¹

EXPERIMENTAL

General remarks. Melting points were determined in a capillary using a *MEL-TEMP II* apparatus (Aldrich) and are uncorrected. IR spectra were recorded in KBr pellets or as films with a *Nexus* spectrophotometer. ^1H -NMR, ^{13}C -NMR, and ^{31}P -NMR spectra were registered in CDCl_3 on a *Tesla BS 687* instrument (^1H at 80 MHz) or a *Bruker AC-300* spectrometer (^1H at 300, ^{13}C at 75, and ^{31}P at 121 MHz, resp.) using TMS ($\delta = 0$ ppm) as an internal and 85% H_3PO_4 as an external standard. ^{13}C -NMR peak assignments were made on the basis of DEPT measurements. MS (CI) were recorded on a *Finnigan-Mat-90* or *Finnigan-SSQ-700* spectrometer; m/z (rel.%). Elemental analyses were performed in the Analytical Laboratory of the University of Zürich.

Starting materials. Ethyl diazomethanephosphonate (**1**) was prepared by the *Seyferth* method.²¹ 2,2,4,4-Tetramethyl-3-thioxocyclobutanone (**6a**),²² 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**6b**),²² 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (**6c**),¹¹ 2-adamantanethione (**6e**),²³ 1,1,3,3-tetramethylindan-2-thione (**6d**),²⁴ 2,2,6,6-tetramethylcyclohexanethione (**6g**),²⁵ thiofenchone (**6f**),²⁶ and thiocamphor (**6h**)²⁶ were synthesized by thionation of corresponding ketones following the literature procedure.

Reactions of thioketones 6a–d with diethyl diazomethanephosphonate (1); isolation of thiiranes 7a–d.

General procedure. A solution of the corresponding thione **6** (1 mmol) and **1** (1 mmol) in dry THF (1

mL) was heated under reflux for 1 h (5 h in the case of **6d**). After evaporation of the solvent, the crude mixtures were analyzed by ^1H -NMR spectroscopy and purified by crystallization. Yields refer to isolated and purified products.

Diethyl (4,4,6,6-tetramethyl-5-oxo-1-thiaspiro[2.3]hexane)-2-phosphonate (7a). Yield: 180 mg (59%). Colorless crystals (hexane); mp 71–73 °C. IR (KBr): 2958s, 2929m, 1783vs (C=O), 1460m, 1442m, 1256s and 1242s (P=O), 1047vs and 1022vs (P–O–C), 971s, 540s. ^1H -NMR (CDCl_3): 1.09 (d, $J_{\text{H,P}} = 1.3$ Hz, Me), 1.27, 1.31, 1.53 (3s, 3 Me), 1.36, 1.37 (2t, $J_{\text{H,H}} = 7.1$ Hz, 2 MeCH₂O), 2.99 (d, $^2J_{\text{H,P}} = 9.4$ Hz, CH), 4.15–4.27 (m, 2 MeCH₂O). ^{13}C -NMR (CDCl_3): 16.4, 16.5 (2d, $^3J_{\text{C,P}} \approx 6.7$ Hz, 2 MeCH₂O), 22.5, 22.7, 23.4, 24.0 (4 Me), 31.5 (d, $^1J_{\text{C,P}} = 192$ Hz, CH), 61.9, 62.3 (2s, 2 C_q), 63.2, 63.4 (2d, $^2J_{\text{C,P}} \approx 6.8$ Hz, 2 MeCH₂O), 65.7 (d, $^2J_{\text{C,P}} = 2.8$ Hz, C_qS), 218.5 (C=O). ^{31}P -NMR (CDCl_3): 20.97. CI-MS (NH_3): 630 (6, $[2\text{M}+\text{NH}_4]^+$), 613 (19, $[2\text{M}+1]^+$), 581 (11), 325 (16), 324 (100, $[\text{M}+\text{NH}_4]^+$), 307 (31). Anal. Calcd for $\text{C}_{13}\text{H}_{23}\text{O}_4\text{PS}$: C, 50.97; H, 7.57; S, 10.47. Found: C, 50.63; H, 7.63; S, 10.15.

Diethyl (4,4,6,6-tetramethyl-5-thioxo-1-thiaspiro[2.3]hexane)-2-phosphonate (7b). Yield: 200 mg (62%). Orange crystals (petroleum ether); mp 82–84 °C. IR (KBr): 2971s, 2953s, 1451m, 1394m, 1299s, 1239vs (P=O), 1107s, 1048vs and 1019vs (P–O–C), 975s, 870m, 541m. ^1H -NMR (CDCl_3): 1.16, 1.33, 1.36, 1.60 (4s, 4 Me), 1.37–1.40 (m, 2 MeCH₂O), 3.03 (d, $^2J_{\text{H,P}} = 9.2$ Hz, CH), 4.16–4.27 (m, 2 MeCH₂O). ^{13}C -NMR (CDCl_3): 16.4, 16.5 (2d, $^3J_{\text{C,P}} \approx 6.7$ Hz, 2 MeCH₂O), 26.3, 26.5, 27.4, 28.1 (4 Me), 32.1 (d, $^1J_{\text{C,P}} = 191$ Hz, CH), 63.2, 63.4 (2d, $^2J_{\text{C,P}} \approx 6.9$ Hz, 2 MeCH₂O), 64.3, 65.5 (2s, 2 C_q), 69.2 (d, $^2J_{\text{C,P}} = 3.0$ Hz, C_qS), 275.9 (C=S). ^{31}P -NMR (CDCl_3): 21.45. CI-MS (NH_3): 340 (8, $[\text{M}+\text{NH}_4]^+$), 325 (10), 323 (100, $[\text{M}+1]^+$), 291 (5). Anal. Calcd for $\text{C}_{13}\text{H}_{23}\text{O}_3\text{PS}_2$: C, 48.43; H, 7.19; S, 19.89. Found: C, 48.34; H, 7.16; S, 19.59.

Diethyl (5,5-dichloro-4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexane)-2-phosphonate (7c). Yield: 220 mg (61%). Colorless crystals (hexane); mp 48–50 °C. IR: 2988s, 2931m, 1466m, 1370m, 1259s and 1244s (P=O), 1054vs and 1030vs (P–O–C), 973s, 920s, 817m, 533m. ^1H -NMR (CDCl_3): 1.13, 1.35, 1.48, 1.69 (4s, 4 Me), 1.36–1.38 (m, 2 MeCH₂O), 2.67 (d, $^2J_{\text{H,P}} = 8.2$ Hz, CH), 4.14–4.23 (m, 2 MeCH₂O). ^{13}C -NMR (CDCl_3): 16.4, 16.5 (2d, $^3J_{\text{C,P}} \approx 6.0$ Hz, 2 MeCH₂O), 26.0, 26.3, 26.9, 27.8 (4 Me), 29.8 (d, $^1J_{\text{C,P}} = 192$ Hz, CH), 54.2 (s, C_q), 55.3 (d, $^3J_{\text{C,P}} = 2.4$ Hz, C_q), 63.0, 63.4 (d, $^2J_{\text{C,P}} \approx 6.8$ Hz, MeCH₂O), 67.1 (d, $J_{\text{C,P}} = 3.0$ Hz, C_qS), 100.0 (s, CCl₂). ^{31}P -NMR (CDCl_3): 21.01. CI-MS (NH_3): 691 (8), 378 (100, $[\text{M}+\text{NH}_3]^+$), 346 (34), 329 (30), 291 (5). Anal. Calcd for $\text{C}_{13}\text{H}_{23}\text{O}_3\text{Cl}_2\text{PS}$: C, 43.22; H, 6.42; S, 8.57. Found: C, 43.17; H, 6.31; S, 8.46.

Diethyl (1,1,3,3-tetramethylindane-2-spiro-2'-thiirane)-3-phosphonate (7d). Yield: 230 mg (65%). Colorless crystals (hexane); mp 80–83 °C. IR: 2975s, 2931m, 1632m, 1483s, 1257s (P=O), 1052vs and

1025vs (P–O–C), 973s, 766s, 756s, 540m, 526m. $^1\text{H-NMR}$ (CDCl_3): 1.13, 1.43, 1.53, 1.64 (4s, 4 Me), 1.34–1.42 (m, 2 MeCH_2O), 2.76 (d, $^2J_{\text{H,P}} = 5.0$ Hz, CH), 4.17–4.31 (m, 2 MeCH_2O), 7.13–7.29 (m, 4 arom. H). $^{13}\text{C-NMR}$ (CDCl_3): 16.4, 16.6 (2d, $^3J_{\text{C,P}} \approx 5.9$ Hz, 2 MeCH_2O), 27.2, 30.3, 30.9, 32.6 (4 Me), 30.7 (d, $^1J_{\text{C,P}} = 194$ Hz, CH), 47.0 (d, $^3J_{\text{C,P}} = 2.0$ Hz, C_q), 48.4 (s, C_q), 62.4, 63.4 (2d, $J_{\text{C,P}} \approx 6.8$ Hz, 2 MeCH_2O), 73.9 (d, $^2J_{\text{C,P}} = 3.0$ Hz, C_qS), 122.0, 122.4, 127.2, 127.6 (4 arom. CH), 147.3, 150.2 (2 arom. C_q). CI-MS (NH_3): 645 (8), 372 (30, $[\text{M}+\text{NH}_4]^+$), 340 (24), 323 (100). Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{O}_3\text{PS}$: C, 60.99; H, 7.68; S, 9.05. Found: C, 60.65; H, 7.66; S, 9.00.

Reactions of thioketones 6b, 6e–6g with diethyl diazomethylphosphonate (1); desulfurization of thiiranes 7e, 8, 12 and 15 with tris(diethylamino)phosphine. General procedure. To a boiling solution of **1** (1 mmol, in the case of **6b**, 3 mmol of **1** were used) in toluene (2–5 mL) was portionally added **6b** or **6e** (1 mmol) in toluene (5–10 mL). The mixtures were heated under reflux for 2–3 h. Thiones **6f** and **6g** and **1** were heated in dry THF (2 mL) for 0.5–2 h. After completion of the reaction and evaporation of the solvent, the crude mixture was crystallized from hexane to give a mixture of thiiranes as a colorless solid. This material was treated with $(\text{Et}_2\text{N})_3\text{P}$ (1.2 mmol) in refluxing dry THF (2 mL) for 2–4 h yielding a 1:4 mixture of *cis*-**9** and *trans*-**9**. The products were separated chromatographically (SiO_2 , hexane/ AcOEt : 3.5:1.5). In the case of **6b**, an analytically pure sample was obtained after crystallization from hexane in dry ice. Yields refer to isolated and purified products.

Diethyl (*{3-[(diethoxyphosphoryl)methylene]-2,2,4,4-tetramethylcyclobutan-1-ylidene}methanephosphonate (9)*). After layer chromatography, a single isomer of **9**, i.e., *trans*-**9**, was isolated. Yield: 200 mg (51%). Colorless crystals (hexane); mp 80–82 °C. IR: 2983m, 2961m, 1634s, 1249vs (P=O), 1050vs and 1030vs (P–O–C), 964s, 855m, 823m, 553m. $^1\text{H-NMR}$ (CDCl_3): 1.33 (t, $J_{\text{H,H}} = 7.1$ Hz, 2 MeCH_2O), 1.49 (s, 4 Me), 4.06 (quint-like, $J_{\text{H,H}} \approx J_{\text{H,P}} \approx 7$ Hz, 2 MeCH_2O), 5.45 (d, $J_{\text{H,P}} = 14.0$ Hz, 2 =CH). $^{13}\text{C-NMR}$ (CDCl_3): 16.2 (d, $^3J_{\text{C,P}} = 6.4$ Hz, 2 MeCH_2O), 25.9 (4 Me), 52.1 (dd, $^3J_{\text{C,P}} = 22.4$ and 8.7 Hz, 2 C_q), 61.2 (d, $^2J_{\text{C,P}} = 5.4$ Hz, 2 MeCH_2O), 105.4 (d, $^1J_{\text{C,P}} = 192.2$ Hz, =CH), 182.4 (s, C_q). $^{31}\text{P-NMR}$ (CDCl_3): 16.93. CI-MS (NH_3): 410 (20), 409 (100, $[\text{M}+1]^+$). Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{O}_6\text{P}_2$: C, 52.94; H, 8.39. Found: C, 52.47; H, 8.33.

Diethyl (*adamantan-2-ylidene*)methanephosphonate (**11**). Yield: 160 mg (56%). Colorless, thick oil. IR: 2980m, 2907s, 2852m, 1625m, 1450m, 1244s (P=O), 1055vs and 1028vs (P–O–C), 961s, 819m. $^1\text{H-NMR}$ (CDCl_3): 1.32 (t, $J_{\text{H,H}} = 7.1$ Hz, 2 MeCH_2O), 1.78–1.90, 1.90–2.02 (2m, 12 H), 2.48 (br s, 1 H), 3.50 (br s, 1 H), 4.06 (quint-like, $J_{\text{H,H}} \approx J_{\text{H,P}} \approx 7$ Hz, 2 MeCH_2O), 5.27 (d, $J_{\text{H,P}} = 20.5$ Hz, =CH). $^{13}\text{C-NMR}$ (CDCl_3): 16.3 (d, $^3J_{\text{C,P}} = 6.6$ Hz, 2 MeCH_2O), 27.6 (2 CH), 35.2 (d, $^3J_{\text{C,P}} \approx 7$ Hz, CH), 36.6, 39.1, 39.8 (4 CH_2),

42.5 (*d*, $^3J_{C,P} \approx 25$ Hz, CH), 61.0 (2 MeCH₂O), 103.6 (*d*, $^1J_{C,P} = 187.9$ Hz, =CH), =C not detected. ^{31}P -NMR (CDCl₃): 19.58. CI-MS (NH₃): 286 (17), 285 (100, $[M+1]^+$). Anal. Calcd for C₁₅H₂₅O₃P: C, 63.36; H, 8.86. Found: C, 63.43; H, 8.90.

Diethyl (1,3,3-trimethylbicyclo[2.2.1]heptan-2-ylidene)methanephosphonate (13). A 4:1 mixture of isomeric compounds **13** (*Z*- and *E*- attribution is unknown) was obtained as the crude product. Yield: 200 mg (70%). After column chromatography (SiO₂), a single isomer of **13** was isolated as yellowish, thick oil. IR (neat): 2977s, 2961s, 1626m, 1240s (P=O), 1055vs and 1030vs (P–O–C), 961s, 823m. ^1H -NMR (CDCl₃): 1.05, 1.07, 1.57 (3s, 3 Me), 1.25 (*d*-like, 2 H), 1.33 (*t*, $J_{H,H} = 7.1$ Hz, 2 MeCH₂O), 1.40–1.95 (*m*, 5 H), 4.00–4.14 (*m*, 2 MeCH₂O), 5.23 (*d*, $J_{H,P} = 14.0$ Hz, =CH). ^{13}C -NMR (CDCl₃): 16.2 (*d*, $^3J_{C,P} = 6.7$ Hz, 2 MeCH₂O), 19.2, 26.3, 28.6 (3 Me), 25.1, 35.0, 46.0 (3 CH₂), 46.4 (CH), 47.4 (*d*, $^3J_{C,P} = 19.3$ Hz, C_q), 52.3 (*s*, C_q), 61.0 (*d*, $^3J_{C,P} = 22.3$ Hz, 2 MeCH₂O), 102.3 (*d*, $^1J_{C,P} = 197.0$ Hz, =CH), =C not detected. ^{31}P -NMR (CDCl₃): 20.00. CI-MS (NH₃): 288 (17), 287 (100, $[M+1]^+$), 286 (7).

Diethyl (2,2,6,6-tetramethylcyclohexylidene)methanephosphonate (16). Yield: 150 mg (53%). Yellowish, thick oil. IR (neat): 2962s, 2932s, 2870m, 1585m, 1467m, 1389m, 1366m, 1243s (P=O), 1056vs and 1030vs (P–O–C), 958s, 784m, 567m. ^1H -NMR (CDCl₃): 1.18, 1.42 (2s, 4 Me), 1.327, 1.328 (2*t*, $J_{H,H} = 7.0$ Hz, 2 MeCH₂O), 1.45–1.55 (*m*, 4 H), 1.60–1.68 (*m*, 2 H), 4.00–4.12 (*m*, 2 MeCH₂O), 5.63 (*d*, $J_{H,P} = 8.1$ Hz, =CH). ^{13}C -NMR (CDCl₃): 16.2 (*d*, $^3J_{C,P} = 6.6$ Hz, 2 MeCH₂O), 17.6 (CH₂), 30.4, 32.4 (2 Me), 37.6 (*s*, C_q), 38.5, 40.9 (2 CH₂), 39.5 (*d*, $^3J_{C,P} \approx 7$ Hz, C_q), 61.0 (*d*, $^3J_{C,P} = 6.2$ Hz, 2 MeCH₂O), 110.0 (*d*, $^1J_{C,P} = 192.7$ Hz, =CH), =C not detected. ^{31}P -NMR (CDCl₃): 20.36. CI-MS (NH₃): 290 (17), 289 (100, $[M+1]^+$). Anal. Calcd for C₁₅H₂₉O₃P: C, 62.48; H, 10.14. Found: C, 62.19; H, 9.86.

Reaction of 2,2,6,6-tetramethylcyclohexanethione (6g) in THF; formation of 17. A solution of **1** (178 mg, 1 mmol) and **6g** (170 mg, 1 mmol) in dry THF (stored for a longer time over sodium, 1 mL) was heated under reflux for 0.5 h. After evaporation of the solvent, the crude mixture was crystallized from hexane to give *diethyl (6,6,10,10-tetramethyl-4-thia-1,2-diazaspiro[4.5]dec-2-ene)-3-phosphonate (17)*. Yield: 120 mg (35%). Colorless crystals; mp 105–120 °C (decomp.). IR (KBr): 3250s, 2982m, 2959m, 2933m, 2868m, 1526m, 1440m, 1246s (P=O), 1038s (P–O–C), 984m, 961m, 766m, 522m. ^1H -NMR (CDCl₃): 1.01 (*s*, 2 Me), 1.09 (*s*, 2 Me), 1.36 (*t*, $J_{H,H} = 7.0$ Hz, 2 MeCH₂O), 1.40–1.65 (*m*, 3 CH₂), 4.10–4.24 (*m*, 2 MeCH₂O), 6.65 (br *s*, NH). ^{13}C -NMR (CDCl₃): 16.3 (*d*, $^3J_{C,P} = 6.4$ Hz, 2 MeCH₂O), 18.1 (CH₂), 25.2 (2 Me), 29.4 (2 Me), 36.5 (2 CH₂), 41.8 (2 C_q), 63.1 (*d*, $^2J_{C,P} = 5.2$ Hz, 2 MeCH₂O), 100.7 (C_q), 131.6 (*d*, $^1J_{C,P} = 242$ Hz, C_q). ^{31}P -NMR (CDCl₃): 6.6. CI-MS (NH₃): 350 (18), 349 (100, $[M+1]^+$), 321 (5), 264 (7), 223 (6). Anal. Calcd for C₁₅H₂₉N₂O₃PS: C, 51.71; H, 8.39; N, 8.04. Found: C, 51.82; H, 7.90; N, 7.81.

Reaction of thiocamphor (6h) with 1. A solution of **6h** (168 mg, 1 mmol) and **1** (178 mg, 1 mmol) in dry THF (1 mL) was heated under reflux for 6 h. After evaporation of the solvent, the crude mixture was separated chromatographically on a SiO₂ column (CH₂Cl₂/Et₂O 1:1) to give *diethyl [(1,7,7-trimethyl-bicyclo[2.2.1]hept-2-en-2-yl)sulfanyl]methanephosphonate (18)*. Yield: 200 mg (63%). Yellow, thick oil. IR (neat): 2983s, 2954s, 2911s, 1563m, 1474m, 1452m, 1389s, 1375s, 1258s (P=O), 1054s and 1026s (P–O–C), 965s, 827m, 821m. ¹H-NMR (CDCl₃): 0.79, 0.81, 1.01 (3s, 3 Me), 1.10–2.45 (m, 5 H), 1.32 (t, *J*_{H,H} = 7.1 Hz, 2 MeCH₂O), 2.94 (d, ²*J*_{H,P} = 16.0 Hz, CH₂P), 3.95–4.40 (m, 2 MeCH₂O), 5.58 (d, *J*_{H,H} = 4.3 Hz, =CH). ¹³C-NMR (CDCl₃): 125.1 (s, C=CH), 143.5 (d, ³*J*_{C,P} = 7.5 Hz, C=CH). ³¹P-NMR (CDCl₃): 24.09. CI-MS (NH₃): 320 (18), 319 (100, [M+1]⁺), 287 (30). Anal. Calcd for: C₁₅H₂₇O₃PS: C, 56.58; H, 8.55, S, 10.07. Found: C, 56.61; H, 8.56, S, 9.89.

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