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Reactions of Polycyclic Thioketones with a Phosphonylated Carbanion

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ABSTRACT: *Polycyclic, nonenolizable cycloaliphatic thioketones* **1a** *and* **1b** *react smoothly with the lithium salt of diethyl methylphosphonate* **7** *in THF solution at −40°C to afford products of the carbophilic attack exclusively. Quenching of the obtained lithium thiolates with alkyl iodides yields sulfanes of type* **9** *or* **11**, *respectively, in good yields. 1-Fluoro-2,4-dinitrobenzene was shown to act as an arylating agent. In the case of the "cage" thioketone* **1b**, *the carbanion of salt* **7** *approaches the C=S bond from the exo-side exclusively. In contrast to the parent carbonyl compounds, thioketones* **1** *show no tendency to undergo the conversion analogous to the Horner–Wadsworth–Emmons reaction, which would result in the formation of an olefinic product.* © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:182–187, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20390

Dedicated to Prof. M. Mikolajczyk on the occasion of his 70th birthday.

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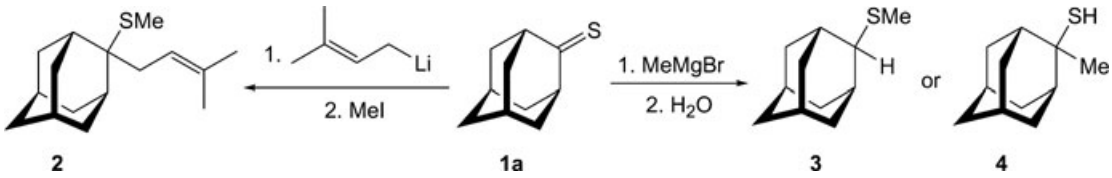
INTRODUCTION

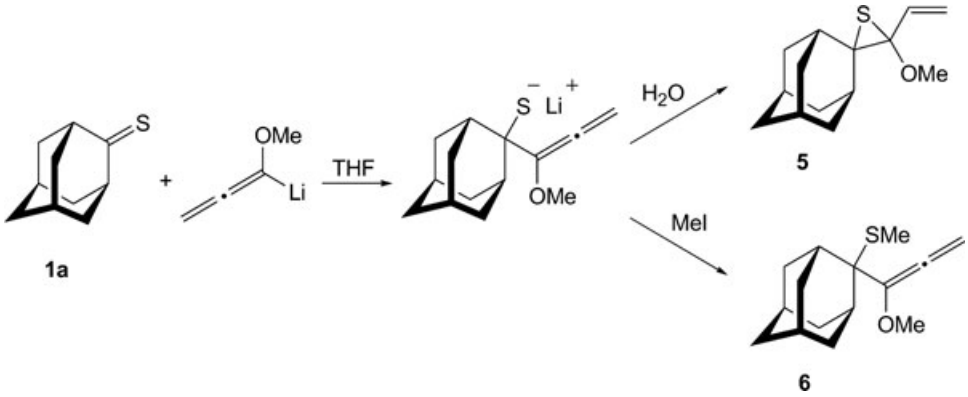
It is well documented that reactions of thioketones with organometallic compounds occur either in a carbophilic or thiophilic fashion [1,2]. Recently, it has been demonstrated that the additions of Grignard reagents with aromatic thioketones proceed via a multistep reaction mechanism, including single electron transfer (SET) processes [3]. In the case of adamantanethione (**1a**), the addition of prenyllithium occurs in a carbophilic manner, and the quenching with methyl iodide leads to the corresponding methyl sulfane **2** [4] (Scheme 1).

On the other hand, the course of the addition with methylmagnesium bromide strongly depends on the solvent used: whereas the thiophilic addition to give **3** is observed in THF, the use of diethyl ether is reported to lead to product **4** of the carbophilic addition [5]. In the same paper, the reaction of **1a** with vinylmagnesium bromide is reported to yield the product of the carbophilic addition exclusively (cf. [6]). The reaction with 1-methoxyallenyllithium occurs in the carbophilic mode and leads to the corresponding 2-allenyladamantane-2-thiolate, which after quenching with water yields thiirane **5** as a product of an intramolecular nucleophilic addition (Scheme 2). The quenching with methyliodide gives the expected methylsulfane **6** [7].

Phosphonylated carbanions are widely applied in reactions with carbonyl compounds [8],



SCHEME 1



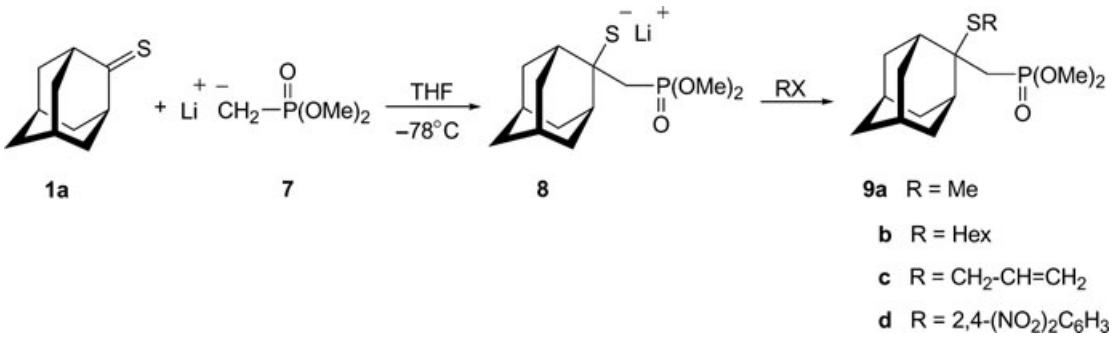
SCHEME 2

but no reactions with thiocarbonyl derivatives have been reported to date. In the present paper, the first results of the reactions of the carbanion generated from dimethyl methylphosphonate with the polycyclic thioketone **1a** (adamantanethione) and the recently prepared "cage" thioketone **1b** (pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8-thione) [9] are described.

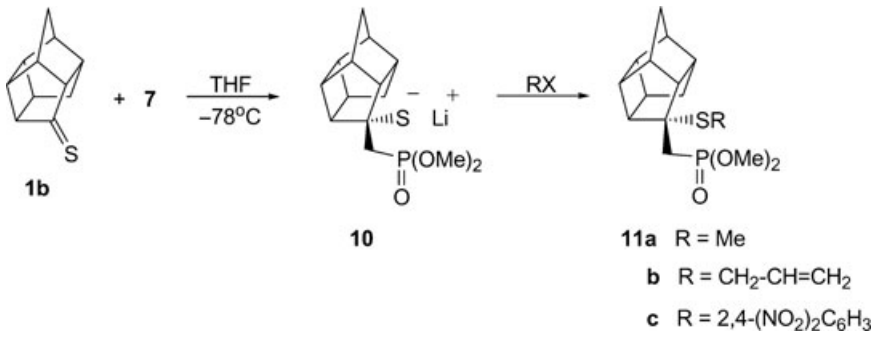
RESULTS AND DISCUSSION

In a typical procedure, dimethyl methylphosphonate in THF was treated with butyl lithium at −78°C to generate the corresponding salt **7**. After addition of a solution of adamantanethione (**1a**) in THF, the initially red mixture decolorized during the warming at about −20°C. At this temperature, the in situ formed thiolate was quenched by the addition of excess methyl iodide and slowly warmed up to room temperature. After workup, the ^{1}H NMR analysis showed the presence of only one methylated product with the characteristic absorption of the MeS group at 1.96 ppm. In the ^{13}C NMR spectrum, the corresponding signal appeared at 9.4 ppm. After column chromatography (silica gel), the product was isolated in 49% yield as a yellowish oil, which subsequently crystallized as yellow needles. On the basis of the spectroscopic data and elemental analyses, the structure **9a** was confirmed (Scheme 3).

Using the same procedure, the replacement of methyl iodide by hexyl iodide, allyl iodide, and 2,4-dinitrofluorobenzene, respectively, afforded the



SCHEME 3



SCHEME 4

(2-sulfanyladamantan-2-yl)methyl phosphonates **9b–d** in good yields. The attempted alkylations of **8** with either bromo- or chloroacetates, as well as the arylation with 2,4-dinitrochlorobenzene, did not take place.

The reactions of the carbanion **7** with the "cage" thioketone **1b**, followed by quenching with methyl iodide, resulted in the formation of only one stereoisomer of the 1:1:1 adduct. Tentatively, the structure of this product was proposed as the *endo* methylsulfanyl derivative **11a** (Scheme 4). In analogy to the series of compounds **9**, the thiolate **10**, upon treatment with allyl iodide and 2,4-dinitrofluorobenzene, was transformed into **11b** and **11c**, respectively. In contrast to the adamantane derivatives **9**, the H-atoms of the CH_2P group are diastereotopic and, therefore, appear in the ^1H NMR spectra as an AB system with an additional H,P coupling. The MeO groups of **11** are also diastereotopic and show two separate absorptions split into doublets by the coupling with the P-atom.

The yellow crystals of **11c** were suitable for an X-ray crystal-structure determination, which confirmed the proposed structure (Fig. 1). By analogy, it is likely that the sulfanyl groups of **11a** and **11b** are also *endo* oriented.

Three facts of the present study are worthy of emphasis. First, the addition of **7** to the thioketones **1a** and **1b** occurs selectively in a carbophilic fashion. Second, the nucleophilic attack of **7** onto the C=S group of **1b** proceeds, as expected [11,12], from the *exo* side. Finally, in contrast to the corresponding reactions with ketones (the Horner–Wadsworth–Emmons olefination of adamantanone is well documented [13,14]), the initially formed thiolates of type **8** and **10** are stable in solution and do not undergo further elimination of a thiophosphonate molecule. Therefore, instead of olefins, the substituted alkylphosphonates are obtained. However, it is worth mentioning that the Wittig reaction of

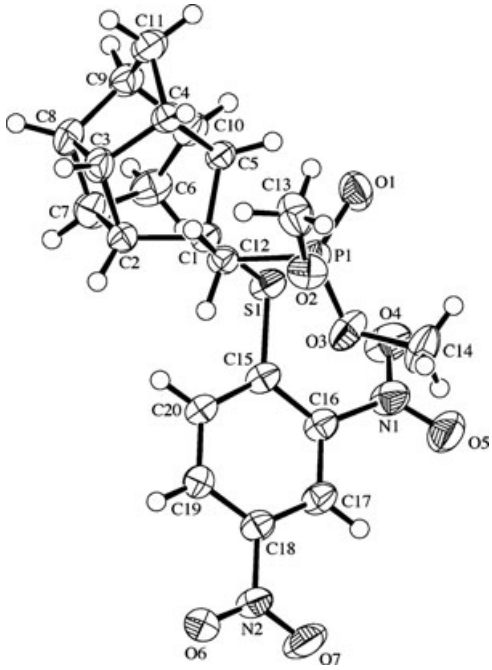


FIGURE 1 ORTEP-plot [10] of the molecular structure of one of the two symmetry-independent molecule in the crystals of **11c** (50% probability ellipsoids; arbitrary numbering of atoms).

1a with triphenylphosphonium methylide leads to spiro[adamantane-2,2'-thiirane] [15,16].

EXPERIMENTAL

General

The ^1H NMR (300 MHz), ^{31}P NMR (121 MHz), and ^{13}C NMR (75 MHz) spectra were recorded using a Bruker AC-300 spectrometer. ^{13}C NMR Assignments were made on the basis of DEPT experiments. The IR spectra were recorded using an FT-IR Nexus spectrophotometer. The mass spectra were obtained using a LKB-2091 spectrometer.

Materials

Adamantanthione (**1a**) [17] and pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-thione (**1b**) [9,18] were prepared according to known protocols. The commercial dimethyl methylphosphonate was distilled prior to the use. Commercial solution of *n*-butyllithium in hexane (2.5 M) was purchased from Sigma-Aldrich.

Reactions of Thioketones **1** *with Lithium Dimethyl Methylphosphonate: General Procedure.* To a solution of dimethyl methylphosphonate (1.5 mmol, 186 mg) in dry THF (4 mL) under argon at −78°C, a solution of *n*-butyllithium in hexane (0.5 mL, 1.25 mmol) was added dropwise. The reaction mixture was stirred for 30 min. Then, the solution of **1a** or **1b** (1 mmol) in anhydrous THF (1 mL) was added dropwise. The initially red solution decolorized during warming to about −20°C. The mixture was quenched by adding an alkylating or arylating agent (1.3 mmol), allowed to warm to room temperature and was treated with water. The solution was extracted with dichloromethane and the organic layers were combined and dried over anhydrous $MgSO_4$. After filtration, the solvents were evaporated and the crude product was purified by column chromatography on silica gel using dichloromethane with an increasing amount of methanol (0%–5%) as an eluent.

*Dimethyl {[2-(Methylsulfanyl)adamantan-2-yl] methyl}phosphonate (***9a***).* The product was isolated as yellow oil. Yield: 360 mg (49%). Crystallization from hexane gave pure **9a** as yellowish crystals (mp 61°C–63°C). IR (KBr): *ν* 2943, 2918, 2900, 2858, 2845, 2668, 2637, 1636, 1455, 1241, 1063, 1049, 1040, 1033, 810, 801 cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 1.52–2.07 (m, 14H, CH, CH_2), 1.96 (s, 3H, CH_3S), 2.58 (d, $^2J_{H,P}$ = 19.7 Hz, 2H, CH_2P), 3.75 [d, $^3J_{H,P}$ = 10.9 Hz, 6H, $(CH_3O)_2P$] ppm. ^{13}C NMR ($CDCl_3$): *δ* = 9.4 (CH_3S), 27.3, 27.4, 34.3, 34.5 (4CH), 32.8, 33.1, 39.2 ($5CH_2$), 32.6 (d, $^1J_{C,P}$ = 147.9 Hz, CH_2P), 51.2 (d, $^2J_{C,P}$ = 3.6 Hz, C_q), 52.1 [d, $^2J_{C,P}$ = 6.6 Hz, $(CH_3O)_2P$] ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): *δ* 30.53 ppm. MS-CI (NH_3) *m/z* (%): 305 (100) $[M + 1]^+$, 257 (28) $[(M + 1) - SCH_3]^+$. Anal. Calcd for $C_{14}H_{25}O_3PS$ (304.39): C, 55.24; H, 8.28; S, 10.53; found: C, 55.14; H, 8.02; S, 10.59.

*Dimethyl {[2-(Hexylsulfanyl)adamantan-2-yl] methyl}phosphonate (***9b***).* The product was isolated as brown oil. Yield: 740 mg (82%). Crystallization from hexane at low temperature (dry ice) gave pure **9b** as brownish crystals, which melted at room temperature. IR (film): *ν* 2919, 2852, 2669, 2654, 2638, 1749, 1718, 1653, 1635, 1455, 1281, 1252, 1182, 1097, 1063, 1035, 963, 901, 872, 805 cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 0.89 (t, $^3J_{H,H}$ = 6.8 Hz, 3H, CH_3), 1.25–2.20 (m, 20H, CH, CH_2), 2.41 (t, $^3J_{H,H}$ = 7.3 Hz, 2H, CH_2S), 2.50–2.65 (m with d at 2.55, $^2J_{H,P}$ = 19.7 Hz, 4H, CH_2P, CH_2), 3.75 [d, $^3J_{H,P}$ = 10.9 Hz, 6H, $(CH_3O)_2P$] ppm. ^{13}C NMR ($CDCl_3$): *δ* 14.1 (CH_3), 33.0, 33.2, 39.3 ($5CH_2$), 22.6, 26.5, 29.2, 29.7, 31.6 ($5CH_2$), 27.4, 27.5, 34.9, 35.0 (4 CH), 33.7 (d, $^1J_{C,P}$ = 147.6 Hz, CH_2P), 52.1 [d, $^2J_{C,P}$ = 6.7 Hz, $(CH_3O)_2P$], 52.2 (d, $^2J_{C,P}$ − 3.3 Hz, C_q) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): *δ* 28.85 ppm. MS-CI (NH_3) *m/z* (%): 375 (100) $[M + 1]^+$, 257 (67) $[(M + 1) - S(CH_2)_5CH_3]^+$. Anal. Calcd for $C_{19}H_{35}O_3PS$ (374.52): C, 60.93; H, 9.42; S, 8.56; found: C, 60.97.14; H, 9.29; S, 8.44.

*Dimethyl {[2-(Allylsulfanyl)adamantan-2-yl] methyl}phosphonate (***9c***).* The product was isolated as yellow oil. After heating with charcoal and crystallization from hexane, pure **9c** (500 mg, 63%) was obtained as colorless crystals (mp 41°C–44°C). IR (KBr): *ν* 3075, 3004, 2950, 2935, 2906, 2847, 2669, 2655, 2638, 1635, 1474, 1454, 1437, 1283, 1248, 1180, 1097, 1065, 1049, 1037, 901, 872, 806, 753 cm^{-1}. ^1H NMR ($CDCl_3$): *δ* = 1.53–2.15 (m, 12H, CH, CH_2), 2.54–2.64 (m with d at 2.57, $^2J_{H,P}$ = 19.7 Hz, 4H, CH_2P, CH_2), 3.14 (d, $^3J_{C,H}$ = 7.1 Hz, 2H, CH_2S), 3.76 [d, $^3J_{H,P}$ = 10.9 Hz, 6H, $(CH_3O)_2P$], 5.05–5.23 (m, 2H, $=CH_2$), 5.83–5.94 (m, 1H, =CH) ppm. ^{13}C NMR ($CDCl_3$): *δ* = 30.5 (CH_2S), 27.3, 27.4, 34.9, 35.1 (4CH), 32.9, 33.1, 39.2 ($5CH_2$), 33.8 (d, $^1J_{C,P}$ = 147.8 Hz, CH_2P), 52.2 [d, $^2J_{C,P}$ = 6.6 Hz, $(CH_3O)_2P$], 53.0 (d, $^2J_{C,P}$ = 3.8 Hz, C_q), 117.3 ($=CH_2$), 134.4 (=CH) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): *δ* = 31.46 ppm. MS-CI (NH_3) *m/z* (%): 331 (100) $[M+1]^+$, 257 (82) $[(M + 1) - SCH_2CH{=}CH]^+$. Anal. Calcd for $C_{16}H_{27}O_3PS$ (330.43): C, 58.16; H, 8.24; S, 9.70; found: C, 57.99; H, 8.41; S, 9.82.

*Dimethyl ({2-[(2,4-Dinitrophenyl)sulfanyl] adamantan-2-yl}methyl)phosphonate (***9d***).* The product was isolated as yellow oil. Yield: 640 mg (59%). Crystallization from CH_2Cl_2/hexane gave pure **9d** as yellow crystals (mp 169°C–171°C). IR (KBr): *ν* 3140, 3090, 2945, 2931, 2856, 1636, 1590, 1533, 1515, 1457, 1345, 1248, 1179, 1149, 1063, 1050, 1023, 891, 832, 797, 739 cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 1.69–2.38 (m, 12H, CH, CH_2), 2.60–2.67 (m, with d for CH_2P at 2.64, $^2J_{H,P}$ = 20.4 Hz, 4H), 3.62 [d, $^3J_{H,P}$ = 10.9 Hz, 6H, $(CH_3O)_2P$], 7.81–8.76 (m, 3 arom. H) ppm. ^{13}C NMR ($CDCl_3$): *δ* 26.8, 26.8, 36.9, 37.0 (4 CH), 32.6 (d, $^1J_{C,P}$ = 147.1 Hz, CH_2P), 33.2, 33.7, 38.7 ($5CH_2$), 52.2 [d, $^2J_{C,P}$ = 6.7 Hz, $(CH_3O)_2P$], 53.0 (d, $^2J_{C,P}$ = 4.3 Hz, C_q), 129.7, 125.5, 132.6 ($3CH_{ar}$), 142.7, 144.7, 150.5 (3 arom.

C_q) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 29.05 ppm. MS-CI (NH_3) *m/z* (%): 474 (5), 457 (7) $[M + 1]^+$, 257 (100) $[(M + 1) - SC_6H_3(NO_2)_2]^+$. Anal. Calcd for $C_{19}H_{25}O_7N_2PS$ (456.46): C, 50.00; H, 5.52; N, 6.14; S, 7.02; found: C, 49.74; H, 5.54; N, 6.16; S, 7.00.

*Dimethyl {[8-(Methylsulfanyl)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-yl]methyl}phosphonate (***11a***).* After column chromatography (SiO_2, dichloromethane with an increasing amount of methanol), the product was isolated as a pale yellow oil. Yield: 360 mg (76%). IR (film): υ 2952, 2861, 1740, 1645, 1451, 1408, 1313, 1277, 1248, 1183, 1061, 1031, 888, 866, 794 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.95–1.01 (m, 1H), 1.21, 1.67 (AB, J_{AB} = 10.6 Hz, 2H, CH_2), 1.86–2.74 (m, 10H, CH_2, CH, CH_2P), 2.13 (s, 3H, CH_3S), 3.13 (d, $^1J_{H,P}$ = 12.2 Hz, 1H), 3.73 (d, $^3J_{H,P}$ = 10.9 Hz, 3H, CH_3O), 3.74 (d, $^3J_{H,P}$ = 10.9 Hz, 3H, CH_3O) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.1 (CH_3S), 28.3, 33.0 ($2CH_2$), 36.8 (d, $^4J_{C,P}$ = 2.7 Hz, CH), 37.4 (d, $^1J_{C,P}$ = 144.1 Hz, CH_2P), 44.1 (d, $^3J_{C,P}$ = 14.2 Hz, CH), 41.6, 42.3, 42.8, 45.4, 47.5 (5CH), 48.7 (d, $^3J_{C,P}$ = 6.4 Hz, CH), 51.3 (d, $^2J_{C,P}$ = 3.4 Hz, C_q), 51.9 (d, $^2J_{C,P}$ = 6.7 Hz, 1 CH_3O), 52.1 (d, $^2J_{C,P}$ = 6.6 Hz, 1 CH_3O) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 30.84 ppm. MS-CI (NH_3) *m/z* (%): 316 (18), 315 (100) $[M + 1]^+$, 301 (7), 267 (42) $[M - SCH_3]^+$, 191 (6). Anal. Calcd for $C_{15}H_{23}O_3PS$ (314.39): C, 57.31; H, 7.37; S, 10.20; found: C, 57.26; H, 7.33; S, 10.15.

*Dimethyl {[8-(Allylsulfanyl)pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-yl]methyl}phosphonate (***11b***).* The crude product was isolated as a brownish oil, which after crystallization from hexane (dry ice) gave 250 mg (74%) of the analytically pure **11b** (mp 46°C–48°C). IR (KBr): υ 3079, 2998, 2972, 2963, 2934, 2860, 1635, 1452, 1425, 1415, 1277, 1250, 1237, 1189, 1060, 1045, 1033, 889, 866, 825, 811, 788 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.95–1.02 (m, 1H), 1.21, 1.67 (AB, J_{AB} = 10.6 Hz, 2H, CH_2), 1.86–2.73 (m, 10H, CH, CH_2), 3.12–3.32 (m, 3H), 3.58 [d, $^3J_{H,P}$ = 10.9 Hz, 3H, $(CH_3O)_2P$], 3.60 [$^3J_{H,P}$ = 11.0 Hz, 3H, $(CH_3O)_2P$], 5.04–5.22 (m, 2H, $=CH_2$), 5.38–5.96 (m, 1H, =CH) ppm. ^{13}C NMR ($CDCl_3$): δ 28.3, 33.0 ($2CH_2$), 33.9 (CH_2S), 36.8 (d, $^4J_{C,P}$ = 2.9 Hz, CH), 38.0 (d, $^1J_{C,P}$ = 144.1 Hz, CH_2P), 41.6, 42.3, 42.8, 45.2, 47.6 (5CH), 44.3 (d, $^3J_{C,P}$ = 14.4 Hz, CH), 49.1 (d, $^3J_{C,P}$ = 6.1 Hz, CH), 51.9 (C_q), 52.0, 52.2 [2d, $^2J_{C,P}$ = 6.4 and 6.7 Hz, resp., $(CH_3O)_2P$], 116.9 ($=CH_2$); 135.2 (=CH) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 31.81 ppm. MS-CI (NH_3) *m/z* (%): 331 (100) $[M + 1]^+$, 315 (70), 267 (60) $[(M + 1) - SCH_2CH{=}CH]^+$, 157 (6). Anal. Calcd for $C_{17}H_{25}O_3PS$ (340.42): C, 59.98; H, 7.40; S, 9.42; found: C, 59.73; H, 7.44; S, 9.44.

*Dimethyl ({8-[(2,4-Dinitrophenyl)sulfanyl]pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-yl}methyl)phosphonate (***11c***).* The crude product was isolated as a pale yellow oil, which after crystallization from of hexane/CH_2Cl_2 gave 355 mg (76%) of **11c** as yellow crystals (mp 159°C–160°C). IR (KBr): υ 3101, 2968, 2866, 1593, 1515, 1456, 1403, 1344, 1249, 1048, 1032, 918, 901, 833, 809, 736 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.09–1.15 (m, 1H), 1.31, 1.77 (AB, J_{AB} = 10.8 Hz, 2H, CH_2), 1.86–2.10 (m, 3H, CH, CH_2), 2.36–3.00 (m, 9H, CH, CH_2P); 3.58 [d, $^3J_{H,P}$ = 10.9 Hz, 3H, $(CH_3O)_2P$], 3.60 [d, $^3J_{H,P}$ = 11.0 Hz, 3H, $(CH_3O)_2P$], 7.89–8.84 (m, 3 arom. H) ppm. ^{13}C NMR ($CDCl_3$): δ 28.4, 32.8 ($2CH_2$), 35.2 (d, $^1J_{C,P}$ = 144.9 Hz, CH_2P), 36.5, 41.6, 44.3, 45.6, 45.8, 47.5 (6CH), 42.4 (d, $^3J_{C,P}$ = 4.7 Hz, CH), 50.5 (d, $^3J_{C,P}$ = 5.6 Hz, CH), 52.09, 52.14 (2d, $^2J_{C,P}$ = 6.6 Hz, $(CH_3O)_2P$), 57.3 (C_q), 121.0, 125.8, 131.7 ($3CH_{ar}$), 144.1, 144.4, 148.7 (3 arom. C_q) ppm. ^{31}P NMR ($CDCl_3$, 121 MHz,): δ 28.98 ppm. MS-CI (NH_3): *m/z* (%): 484 (16), 467 (47) $[M + 1]^+$, 267 (100) $[(M + 1) - SC_6H_3(NO_2)_2]^+$, 253 (8). Anal. Calcd for $C_{20}H_{23}O_7N_2PS$ (466.45): C, 51.50; H, 4.97; N, 6.01; S, 6.87; found: C, 51.30; H, 4.83; N, 5.89; S, 6.91.

X-Ray Crystal-Structure Determination of **11c** (Fig. 1). All measurements were made on a Nonius KappaCCD diffractometer [19] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [20]. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multiscan method [21] was applied. A view of the molecule is shown in Fig. 1. The structure was solved by direct methods using SIR92 [22], which revealed the positions of all non-hydrogen atoms. There are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the program PLATON [23], but none could be found. The non-hydrogen 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 Me groups). Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. One reflection, whose intensity was considered to be extreme outliers, was omitted from the final refinement. Neutral atom scattering factors for non-hydrogen atoms were taken from [24], and

the scattering factors for H-atoms were taken from [25]. Anomalous dispersion effects were included in F_c [26]; the values for f' and f' were those of [27]. The values of the mass attenuation coefficients are those of [28]. All calculations were performed using the SHELXL97 [29] program. Crystal data for **11c**: $C_{20}H_{23}N_2O_7PS$, $M = 466.44$, yellow, prism, crystal dimensions $0.15 \times 0.25 \times 0.30$ mm, monoclinic, space group $P2_1/c$, $Z = 8$, $a = 18.4313(3)$ Å, $b = 11.0640(2)$ Å, $c = 21.7924(4)$ Å, $\beta = 109.5339(9)^\circ$, $V = 4188.2(1)$ Å^3, $D_X = 1.479$ g·cm^{-3}, μ (Mo K_α) = 0.277 mm^{-1}, $T = 160$ K, ϕ and ω scans, transmission factors (min; max) 0.835; 0.969, $2\theta_{max} = 55^\circ$, total reflections measured 90,879, symmetry independent reflections 9611, reflections with $I > 2\sigma(I)$ 6096, reflections used in refinement 9610, parameters refined 563, R (on F; $I > 2\sigma(I)$ reflections) = 0.0568, $wR(F^2)$ (all reflections) = 0.1565 ($w = (\sigma^2(F_o^2) + (0.0679P)^2 + 2.7995P)^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$), goodness of fit 1.034, final Δ_{max}/σ 0.001, $\Delta\rho$ (max; min) = 0.46; –0.52 eÅ^{-3}.

CCDC-640446 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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