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# Carbanionic Displacement Reactions at Phosphorus: Synthesis and Reactivity of 5,5-Dimethyl-2-oxo-2-(1,3- dithian-2-yl)-1,3,2-dioxaphosphorinane

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**Carbanionic displacement reactions at phosphorus :  
synthesis and reactivity of 5,5-dimethyl-2-oxo-2-(1,3-dithiane-2-yl)-1,3,2-  
dioxaphosphorinane**

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Summary -We describe the formation and reactivity of the lithiated carbanion of 5,5-dimethyl-2-oxo-2-(1,3-dithian-2-yl)-1,3,2-dioxaphosphorinane **3b**. The derived carbanion **2b** is prepared in quantitative yield by internal quench condensation of 1,3-dithiane and 2-chloro-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane **1b** with two equivalents of LDA at low temperature. The carbanion **2b** is reacted with a variety of ketones in one-carbon homologation reaction and a comparison with other reagents is done.

**chlorophosphates / dithiane / LDA / lithiated phosphonate esters / Horner-Wadsworth-Emmons reaction**

**Réactions de substitution nucléophile sur le phosphore :  
synthèse et réactivité du 5,5-diméthyl-2-oxo-2-(1,3-dithiane-2-yl)-1,3,2-  
dioxaphosphorinane**

**Bogdan Iorga, Virginie Mouriès, et Philippe Savignac**

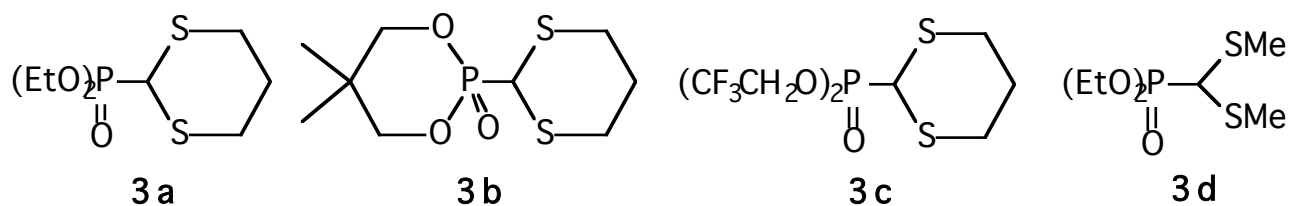
Hétéroéléments et Coordination, URA CNRS 1499, DCPH, Ecole Polytechnique,  
91128 Palaiseau Cedex

Résumé -Nous décrivons la préparation et la réactivité du carbanion lithié dérivé du 5,5-diméthyl-2-oxo-2-(1,3-dithian-2-yl)-1,3,2-dioxaphosphorinane **3b**. Ce carbanion **2b** est préparé quantitativement par addition simultanée du 1,3-dithiane et du 2-chloro-5,5-diméthyl-2-oxo-1,3,2-dioxaphosphorinane **1b** à deux équivalents de LDA à basse température . La réactivité de **1b** est évaluée vis-à-vis des cétones en réaction d'homologation d'un carbone et comparée à celle d'autres réactifs.

**chlorophosphates / dithiane / LDA / carbanion phosphorylé / réaction de Horner-Wadsworth-Emmons**

## Introduction

There is a considerable interest in the synthesis of functional phosphonates, since they have been demonstrated as important precursors in organic synthesis and material science. Several convenient and practical routes to these reagents have been summarized recently<sup>1</sup>. They can be classified into four main categories of reactions : the Michaelis-Arbuzov<sup>2</sup>, Michaelis-Becker<sup>3</sup> and Kinnear-Perren<sup>4</sup> reactions and the addition of trivalent phosphorus reagents at unsaturated carbon<sup>5</sup>. By contrast, generation of a C-P bond by carbanionic displacement of a good leaving group attached at an electropositive quinquivalent phosphorus center has not been yet widely exploited for the preparation of functionalized phosphonates. Our early efforts in this area involved the nucleophilic attack of nitrile-stabilized anions on bis(dimethylamino)chlorophosphate<sup>6</sup> and the reaction of alkylolithiums on trialkylphosphates<sup>7</sup>. More recently, we reported the synthesis and some reactions of diethyl (2-pyridyl)-methylphosphonate<sup>8</sup> which was efficiently accomplished by condensation of the lithiated carbanion of 2-methylpyridine with diethyl chlorophosphate. The carbanionic displacement of chlorine from phosphorus occurs readily at low temperature to generate the carbon-phosphorus bond. An attractive feature in this reaction is the transient formation of an  $\alpha$ -phosphorylated carbanion which is of significant synthetic utility and can be exploited for further reactions and especially for the one-carbon homologation of ketones under the Horner-Wadsworth-Emmons conditions. We now wish to present in details the synthesis and reactivity of 5,5-dimethyl-2-oxo-2-(1,3-dithiane-2-yl)-1,3,2-dioxaphosphorinane **3b** prepared according to the same tactic. To the best of our knowledge, there has been no report concerning formation and reactivity of **3b**. Several thioacetals of formylphosphonates are known, **3a**, **c**, **d** (Scheme 1) and we have undertaken to compare the new **3b** with diethyl 1,3-dithian-2-yl phosphonate **3a**.



Scheme 1

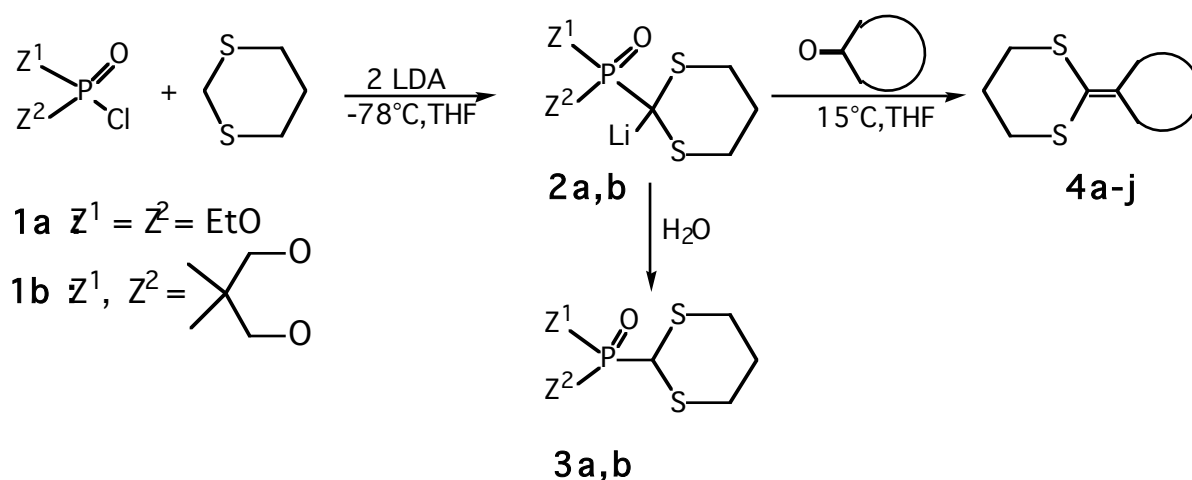
## Results and discussion

Ketene dithioacetals are versatile synthetic intermediates which may be converted by reductive-hydrolysis to aldehydes<sup>9</sup> or by hydrolysis to carboxylic acids derivatives<sup>10</sup>, and consequently a large number of carbonyl olefination reactions have been designed and developed for their preparation<sup>9a,11,12</sup>. The most widely used methods for the synthesis of ketene dithioacetals

involve the Wittig, Horner-Wittig and Horner-Wadsworth-Emmons reactions of  $\alpha$ -phosphoryl dithioacetals with carbonyl compounds<sup>12</sup>. The classical synthesis of  $\alpha$ -phosphoryl dithioacetals is accomplished in high yields by a Michaelis-Arbuzov process involving 2-chloro-1,3-dithiane and a trialkylphosphite<sup>13</sup>. The preparation of the same compounds via the reaction between 2-lithio-1,3-dithiane and chlorophosphines and subsequent oxidation of the resultant phosphine has been reported by Juaristi *et al.*<sup>14</sup>, then with diethyl chlorophosphate by Comins *et al.*<sup>15</sup>. The overall yield of this reaction is modest, and frequently a chromatographic purification is necessary.

We anticipated that dithiane phosphonates could be efficiently prepared by condensation of the derived carbanion of 1,3-dithiane with a chlorophosphate under internal quench conditions. Thus, the generated carbanion is immediately trapped by the electrophile before any possible degradation. In addition, this way offers the possibility to choose the ester substituents of the chlorophosphate so as to modify the reactivity of the phosphoryl group. Two chlorophosphates were tested, the 2-chloro-5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane **1b**, prepared according to the "vacuum process" previously described by us<sup>16</sup>, and the diethyl chlorophosphate **1a** which is a commercially available. The cyclic chlorophosphate **1b** is obtained on molar scale in nearly quantitative yield and used without any purification (m.p. 106-108°C against 63% yield and m.p. 104.5-106°C after recrystallisation<sup>17</sup>). The chlorophosphate **1b** is soluble in acetone, benzene, THF and dichloromethane but insoluble in water, ether and cyclohexane.

The lithiated phosphonate esters **2a** or **2b** were directly obtained by simultaneous addition of a mixture of 1,3-dithiane and chlorophosphate **1a** or **1b** to LDA (2 equiv) in THF at low temperature (internal quench conditions) (Scheme 2). As checked by <sup>31</sup>P-NMR, the result was complete disappearance of the chlorophosphate with clean and complete formation of the stable carbanions **2a** ( $\delta$  <sup>31</sup>P(THF)=45.2) or **2b** ( $\delta$  <sup>31</sup>P(THF)=41.2) which can be kept for a long time at 15°C without decomposition.



**Scheme 2**

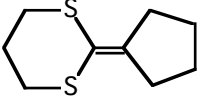
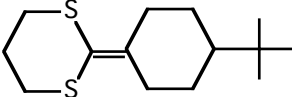
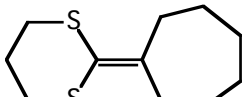
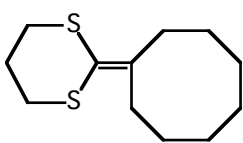
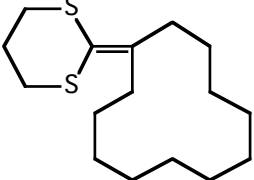
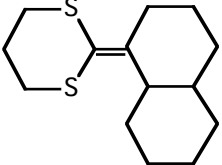
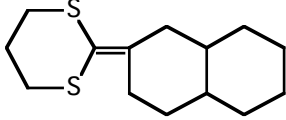
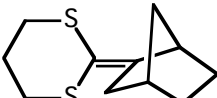
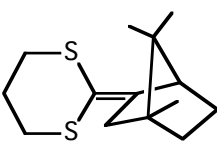
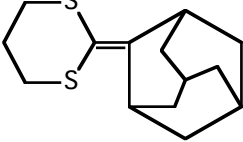
4	Rdt. (%)		
	Route A	Route B	
a		93	65
b		86	82
c		95	
d		92	17
e		93	
f		90	
g		94	
h		90	
i		33	
j		15	

Table 1

After some experimentation, we chose to compare the reactivity of **2a** (route **A**, Table 1) and **2b** (route **B**, Table 1) towards cyclic ketones, sterically hindered or not. Early reported preparations of ketene thioacetals **4** using **1a** included especially aromatic aldehydes<sup>12d,e</sup>, aromatic ketones<sup>12d,e</sup>,  $\alpha,\beta$ -unsaturated aldehydes and ketones<sup>12c</sup>. Recently, the use of 2-phosphoryl 1,3-dithiane bearing trifluoroethyl group on phosphorus **3c** for the direct one-carbon homologation of ketones was described<sup>12a</sup>. One of the attractive feature of **3c** is due to the strong electron withdrawing character of the trifluoroethyl groups which stabilize the derived carbanion, rendering it less basic, and accelerate the elimination step of the Horner-Wadsworth-Emmons reaction<sup>12a</sup>.

We have selected phosphonate **3b** because it is known that modification of the structure of the phosphoryl group in the dithioacetal influences the reactivity of the corresponding carbanion towards ketones<sup>12c</sup>. Cyclic phosphonates are useful intermediates in organic synthesis owing to the enhanced sensitivity of the phosphorus atom to nucleophilic attack. Effectively, on addition of the ketone to **2b** at 15°C, an elevation of temperature was observed (10-15°C). By contrast, the same reaction with **2a** is not so exothermic. On the other hand, reaction time are shorter with **2b** than with **2a**. For example, reaction of cyclopentanone with **2b** needs about 3h against 12h with **2a**<sup>12a</sup>. As shown in Table 1, our experimental results demonstrate that the cyclic phosphorylated anion **2b** is reactive towards a large variety of cyclic ketones mainly due to its less crowded structure which allow an easier approach of the electrophile. The yields are very high, but decrease significantly when the reaction is accomplished with hindered ketones (**4i**, **j**). The evidence is given by the difference of reactivity between norcamphor **4h** and camphor **4i** derivatives. In addition, our attempts in obtaining the corresponding ketene diacetals from 2,6-dimethyl-cyclohexanone and 1-tetralone failed, resulting in complete enolization of the ketone whatever the temperature (-15°C or +15°C).

## Conclusion

Consequently, an efficient synthesis of 5,5-dimethyl-2-oxo-2-(1,3-dithian-2-yl)-1,3,2-dioxaphosphorinane **3b** connected to an easy formation of the corresponding lithiated anion **2b** has been realized. On reaction with cyclic ketones, **2b** has proved to be a good nucleophile able to afford the corresponding ketene thioacetals **4a-j** in high yields. Furthermore, we make a comparison on the opportunity to utilize 5,5-dimethyl-2-oxo-2-chloro-1,3,2-dioxaphosphorinane **1b** or diethyl chlorophosphate **1a** under Horner-Wadsworth-Emmons conditions. It appears clearly that the title compound is the best suited to the synthesis of ketene thioacetals **4**. Moreover the feasibility of the approach encourages the development of related possibilities for C-P bond formation.

## Experimental section

NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200 MHz for proton, 50.3 MHz for carbon and 81.01 MHz for phosphorus. <sup>31</sup>P downfield shifts ( $\delta$ ) are expressed

with a positive sign, in ppm, relative to external 85% H<sub>3</sub>PO<sub>4</sub> in H<sub>2</sub>O. <sup>1</sup>H and <sup>13</sup>C chemical shifts (δ) are reported in ppm relative to CDCl<sub>3</sub> as internal standard. Coupling constants (*J*) are given in Hz. The following abbreviations are used: s, d, t, q, p, m for singlet, doublet, triplet, quadruplet, pentuplet and multiplet respectively. Organic solvents were purified by standard procedures. THF was distilled under an inert atmosphere from purple solutions of sodium-benzophenone ketyl. The synthesis of all compounds were carried out under dry nitrogen.

### General procedure for the synthesis of 2-phosphoryl-1,3-dithiane (3a) or (3b)

An oven-dried, 250 ml, four necked, round-bottomed flask is fitted with an efficient mechanical stirrer, a thermometer, a condenser and a pressure equalizing funnel with a nitrogen inlet. Under a gentle flow of nitrogen the flask is charged with 26.5 ml (42 mmol) of a 1.6M solution of *n*-BuLi in hexane then 4.45 g (44 mmol) of *i*-Pr<sub>2</sub>NH in 20 ml THF is gently added at -78°C. At LDA thus formed, a mixture of **1a** 3.62 g (21 mmol) and 2.4 g (20 mmol) of 1,3-dithiane or **1b** 3.9 g (21 mmol) and 2.4 g (20 mmol) of 1,3-dithiane, dissolved in 50 ml of THF is added at the same temperature. After 30 min. at low temperature, the phosphorylated 1,3-dithiane carbanion **2a** or **2b** obtained is allowed to warm-up at room temperature and hydrolysed with 50 ml of water. For **3a**, the aqueous layer is extracted with Et<sub>2</sub>O (2x20 ml) and the combined organic extracts are dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to afford the crude product which is purified by a silica gel chromatographic column using hexane as eluent. For **3b** the white precipitate is separated from the aqueous layer by filtration and washed with ether.

#### *Diethyl 1,3-dithian-2-yl-phosphonate (3a)*

b.p./torr 129-134°C/0.12<sup>15</sup>

<sup>31</sup>P NMR (CDCl<sub>3</sub>): δ +18.7 (s)

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.38 (t, <sup>3</sup>J<sub>HH</sub>=7, 6H, CH<sub>3</sub>CH<sub>2</sub>O), 1.88-2.23 (m, 2H, CH<sub>2</sub> of 5-dithianyl), 2.50-2.65 (m, 2H, CH<sub>2</sub>(<sub>eq</sub>) of 4,6-dithianyl), 3.45-3.85 (m, 3H, CH<sub>2</sub>(<sub>ax</sub>) of 4,6-dithianyl and CH of 1-dithianyl), 4.28 (p, <sup>3</sup>J<sub>HH</sub>=<sup>4</sup>J<sub>PH</sub>=7, 4H, CH<sub>3</sub>CH<sub>2</sub>O)

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 16.8 (d, <sup>3</sup>J<sub>PC</sub>=5.8, CH<sub>3</sub>CH<sub>2</sub>O), 25.4 (s, CH<sub>2</sub> of 5-dithianyl), 26.5 (s, CH<sub>2</sub> of 4,6-dithianyl), 34.4 (d, <sup>1</sup>J<sub>PC</sub>=160.0, CH of 1-dithianyl), 64.1 (d, <sup>2</sup>J<sub>PC</sub>=7.0, CH<sub>3</sub>CH<sub>2</sub>O)

MS (CI, NH<sub>3</sub>), m/z (relative intensity): 257 (M+1, 100), 274 (M+18, 34)

#### *5,5-dimethyl-2-oxo-2-(1,3-dithian-2-yl)-1,3,2-dioxaphosphorinane (3b)*

m.p. 242-244°C

<sup>31</sup>P NMR (CDCl<sub>3</sub>): δ +13.1(s)

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.10 (s, 3H, CH<sub>3</sub>), 1.15 (s, 3H, CH<sub>3</sub>), 1.85-2.25 (m, 2H, CH<sub>2</sub> of 5-dithianyl), 2.55-2.70 (m, 2H, CH<sub>2</sub>(eq) of 4,6-dithianyl), 3.50-3.85 (m, 2H, CH<sub>2</sub>(ax) of 4,6-dithianyl), 3.85-4.05 (m, 2H, CH<sub>2</sub>(eq)O), 4.20-4.35 (m, 2H, CH<sub>2</sub>(ax)O)

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 22.0 (s, CH<sub>3</sub>), 22.2 (s, CH<sub>3</sub>), 25.5 (s, CH<sub>2</sub> of 5-dithianyl), 26.9 (s, CH<sub>2</sub> of 4,6-dithianyl), 32.7 (d, <sup>1</sup>J<sub>PC</sub>=154.0, CH of 1-dithianyl), 33.2 (d, <sup>3</sup>J<sub>PC</sub>=6, C(CH<sub>3</sub>)<sub>2</sub>), 76.7 (d, <sup>2</sup>J<sub>PC</sub>=6.5, CH<sub>2</sub>O)

MS (CI, NH<sub>3</sub>), m/z (relative intensity): 269 (M+1, 100), 286 (M+18, 9)

### General procedure for the synthesis of ketene thioacetals (4a-j)

The reaction is carried out in the same manner as above. After formation of **2a** or **2b** at low temperature and warming to 15°C a ketone (19 mmol) dissolved in THF is added. After a few hours (about 2 to 4h) at room temperature, the reaction mixture is hydrolysed with 50 ml of water. The aqueous layer is extracted with Et<sub>2</sub>O (2x20 ml) and the combined organic extracts are dried (MgSO<sub>4</sub>) and evaporated under reduced pressure to afford the crude product which is purified by a silica gel chromatographic column using hexane as eluent.

#### *2-Cyclopentylidene-1,3-dithiane (4a)*

Colourless solid, m.p.<45°C

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.60-1.85 (m, 4H, CH<sub>2</sub> of 3,4-cyclopentyl), 2.15 (m, 2H, CH<sub>2</sub> of 5-dithianyl), 2.35-2.50 (m, 4H, CH<sub>2</sub> of 2,5-cyclopentyl), 2.85-3.00 (m, 4H, CH<sub>2</sub> of 4,6-dithianyl)

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 25.9 (s, CH<sub>2</sub> of CH<sub>2</sub> of 5-dithianyl), 27.2 (s, CH<sub>2</sub> of 3,4-cyclopentyl), 30.6 (s, CH<sub>2</sub> of 4,6-dithianyl), 33.7 (s, CH<sub>2</sub> of 2,5-cyclopentyl), 113.9 (s, C<sub>q</sub> of 1-cyclopentyl), 149.7 (s, C<sub>q</sub> of 2-dithianyl)

MS (CI, NH<sub>3</sub>), m/z (relative intensity): 187 (M+1, 100)

#### *2-(4-tert-Butyl-cyclohexylidene)-1,3-dithiane (4b)*

Pale yellow solid, m.p. 66-66.5°C<sup>11d</sup>



$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.80-1.25 (m, 13H,  $\text{CH}_3$  of *t*-Bu and  $\text{CH}_2$  of 3,5-cyclohexyl), 1.65-1.95 (m, 4H,  $\text{CH}_2$  of 2,6-cyclohexyl), 2.10 (m, 2H,  $\text{CH}_2$  of 5-dithianyl), 2.75-2.90 (m, 4H,  $\text{CH}_2$  of 4,6-dithianyl), 3.20 (m, 1H, CH of 4-cyclohexyl)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  25.7 (s,  $\text{CH}_2$  of 5-dithianyl), 29.1 (s,  $\text{CH}_3$  of *t*-Bu), 28.6 (s,  $\text{CH}_2$  of 3,5-cyclohexyl), 30.8 (s,  $\text{CH}_2$  of 4,6-dithianyl), 32.3 (s,  $\text{CH}_2$  of 2,6-cyclohexyl), 32.8 (s, Cq of *t*-Bu), 49.4 (s, CH of 4-cyclohexyl), 115.9 (s, Cq of 1-cyclohexyl), 145.1 (s, Cq of 2-dithianyl)

MS (CI,  $\text{NH}_3$ ),  $m/z$  (relative intensity): 257 (M+1, 100)

#### *2-Cycloheptylidene-1,3-dithiane (4c)*

Pale yellow oil, b.p./torr 160°C/0.3<sup>11e</sup>

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.45–1.65 (m, 8H,  $\text{CH}_2$  of 3,4,5,6-cycloheptyl), 2.13 (m, 2H,  $\text{CH}_2$  of 5-dithianyl), 2.53 (t,  $^3J_{\text{HH}}=6$ , 4H,  $\text{CH}_2$  of 2,7-cycloheptyl), 2.82-2.93 (m, 4H,  $\text{CH}_2$  of 4,6-dithianyl)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  25.2 (s,  $\text{CH}_2$  of 5-dithianyl), 27.5 (s,  $\text{CH}_2$  of 4,5-cycloheptyl), 29.1 (s,  $\text{CH}_2$  of 3,6-cycloheptyl), 30.1 (s,  $\text{CH}_2$  of 4,6-dithianyl), 33.7 (s,  $\text{CH}_2$  of 2,7-cycloheptyl), 119.5 (s, Cq of 1-cycloheptyl), 144.5 (s, Cq of 2-dithianyl)

MS (CI,  $\text{NH}_3$ ),  $m/z$  (relative intensity): 215 (M+1, 100)

#### *2-Cyclooctylidene-1,3-dithiane (4d)*

Pale yellow oil

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.45-1.65 (m, 6H,  $\text{CH}_2$  of 4,5,6-cyclooctyl), 1.65-1.85 (m, 4H,  $\text{CH}_2$  of 3,7-cyclooctyl), 2.20 (m, 2H,  $\text{CH}_2$  of 5-dithianyl), 2.50-2.60 (m, 4H,  $\text{CH}_2$  of 2,8-cyclooctyl), 2.95 (m, 4H,  $\text{CH}_2$  of 4,6-dithianyl)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  25.3 (s,  $\text{CH}_2$  of 5-dithianyl), 26.1 (s,  $\text{CH}_2$  of 5-cyclooctyl), 26.4 (s,  $\text{CH}_2$  of 4,6-cyclooctyl), 27.3 (s,  $\text{CH}_2$  of 3,7-cyclooctyl), 30.0 (s,  $\text{CH}_2$  of 4,6-dithianyl), 33.5 (s,  $\text{CH}_2$  of 2,8-cyclooctyl), 119.2 (s, Cq of 1-cyclooctyl), 145.0 (s, Cq of 2-dithianyl)

MS (CI,  $\text{NH}_3$ ),  $m/z$  (relative intensity): 229 (M+1, 100)

#### *2-Cyclododecylidene-1,3-dithiane (4e)*

White solid, m.p. 127-128°C

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.15–1.75 (m, 18H,  $\text{CH}_2$  of 3,4,5,6,7,8,9,10,11-cyclododecyl), 2.10 (m, 2H,  $\text{CH}_2$  of 5-dithianyl), 2.30–2.50 (m, 4H,  $\text{CH}_2$  of 2,12-cyclododecyl), 2.75–2.90 (m, 4H,  $\text{CH}_2$  of 4,6-dithianyl)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  22.8 (s,  $\text{CH}_2$  of 7-cyclododecyl), 23.8 (s,  $\text{CH}_2$  of 6,8-cyclododecyl), 24.6 (s,  $\text{CH}_2$  of 5,9-cyclododecyl), 25.8 (s,  $\text{CH}_2$  of 5-dithianyl), 26.1 (s,  $\text{CH}_2$  of 4,10-cyclododecyl), 26.2 (s,  $\text{CH}_2$  of 3,11-cyclododecyl), 30.7 (s,  $\text{CH}_2$  of 4,6-dithianyl), 31.1 (s,  $\text{CH}_2$  of 2,12-cyclododecyl), 120.4 (s, Cq of 1-cyclododecyl), 146.5 (s, Cq of 2-dithianyl)

MS (CI,  $\text{NH}_3$ ), m/z (relative intensity): 285 (M+1, 100)

*2-(Decahydronaphthalen-1-ylidene)-1,3-dithiane (mixture of cis-trans isomers) (4f)*

Pale yellow oil, it is a 50/50 mixture of cis and trans isomers

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.85–2.25 (m, 16H, CH of 9,10-decahydronaphthyl and  $\text{CH}_2$  of 3,4,5,6,7,8-decahydronaphthyl and  $\text{CH}_2$  of 5-dithianyl), 2.70–3.10 (m, 6H,  $\text{CH}_2$  of 4,6-dithianyl and  $\text{CH}_2$  of 2-decahydronaphthyl)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  20.9, 21.9, 25.5, 25.8, 26.0, 26.9, 27.0, 27.6, 28.2, 30.6, 30.9, 31.9, 32.1, 33.8 (s,  $\text{CH}_2$  of 2,3,4,5,6,7,8-decahydronaphthyl), 25.6 (s,  $\text{CH}_2$  of 5-dithianyl), 30.5 (s,  $\text{CH}_2$  of 4,6-dithianyl), 36.7, 39.8 (s, CH of 10-decahydronaphthyl), 42.2, 49.2 (s, CH of 9-decahydronaphthyl), 116.6, 118.0 (s, Cq of 1-decahydronaphthyl), 148.0, 148.4 (s, Cq of 2-dithianyl)

MS (CI,  $\text{NH}_3$ ), m/z (relative intensity): 255 (M+1, 100)

*2-(Decahydronaphthalen-2-ylidene)-1,3-dithiane (mixture of cis-trans isomers) (4g)*

Pale yellow oil, it is a 50/50 mixture of cis and trans isomers

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.80–1.90 (m, 12H, CH of 9,10-decahydronaphthyl and  $\text{CH}_2$  of 1,4,5,6,7,8-decahydronaphthyl), 2.00–2.40 (m, 4H,  $\text{CH}_2$  of 5-dithianyl and  $\text{CH}_2$  of 3-decahydronaphthyl), 2.60–3.25 (m, 6H,  $\text{CH}_2$  of 4,6-dithianyl and  $\text{CH}_2$  of 1-decahydronaphthyl)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  22.6, 24.9, 26.5, 26.6, 27.8, 29.0, 29.7, 30.5 (s,  $\text{CH}_2$  of 5,6,7,8-decahydronaphthyl), 25.5 (s,  $\text{CH}_2$  of 5-dithianyl), 30.7 (s,  $\text{CH}_2$  of 4,6-dithianyl), 31.9, 33.5, 34.0, 34.6 (s,  $\text{CH}_2$  of 3,4-decahydronaphthyl), 36.2, 38.5 (s, CH of 10-decahydronaphthyl), 36.4, 39.1 (s,  $\text{CH}_2$  of 1-decahydronaphthyl), 43.4, 43.7 (s, CH of

9-decahydronaphthyl), 116.3, 116.9 (s, Cq of 2-decahydronaphthyl), 143.9, 144.3 (s, Cq of 2-dithianyl)

MS (CI, NH<sub>3</sub>), m/z (relative intensity): 255 (M+1, 100)

*2-(2-(1,3-dithianyliden))norbornane (4h)*

Pale yellow oil crystallized in the cold, m.p. <45°C (37-38°C<sup>9a</sup>)

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.2-1.5 (m, 4H, CH<sub>2</sub> of 5,6-norbornyl), 1.55-1.75 (m, 2H, CH<sub>2</sub> of 5-dithianyl), 1.85-2.35 (m, 4H, CH<sub>2</sub> of 3,7-norbornyl), 2.44 (br s, 1H, CH of 4-norbornyl), 2.5-3.0 (m, 4H, CH<sub>2</sub> of 4,6-dithianyl), 3.26 (br s, 1H, CH of 1-norbornyl)

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 25.8 (s, CH<sub>2</sub> of 5-dithianyl), 28.2, 28.5 (s, CH<sub>2</sub> of 5,6-norbornyl), 30.2, 30.5 (s, CH<sub>2</sub> of 3,7-norbornyl), 36.8 (s, CH of 4-norbornyl), 39.4, 39.7 (s, CH<sub>2</sub> of 4,6-dithianyl), 43.7 (s, CH of 1-norbornyl), 111.4 (s, Cq of 2-norbornyl), 151.0 (s, Cq of 2-dithianyl)

MS (CI, NH<sub>3</sub>), m/z (relative intensity): 213 (M+1, 100)

*2-(2-(1,3-dithianyliden))-1,7,7-trimethylnorbornane (4i)*

Pale yellow oil

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.80-2.20 (m, 17H, CH<sub>3</sub>(<sub>exo</sub>), CH<sub>3</sub>(<sub>endo</sub>) of 7-norbornyl, CH<sub>3</sub> of 1-norbornyl, CH<sub>2</sub> of 5,6-norbornyl, CH<sub>2</sub> of 5-dithianyl, CH of 4-norbornyl and CH<sub>2</sub>(<sub>endo</sub>) of 7-norbornyl), 2.52 (m, 1H, CH<sub>2</sub>(<sub>exo</sub>) of 7-norbornyl), 2.8-2.95 (m, 4H, CH<sub>2</sub> of 4,6-dithianyl)

<sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 16.4 (s, CH<sub>3</sub>(<sub>exo</sub>) of 7-norbornyl), 19.6 (s, CH<sub>3</sub> of 1-norbornyl), 20.8 (s, CH<sub>3</sub>(<sub>endo</sub>) of 7-norbornyl), 25.8 (s, CH<sub>2</sub> of 5-dithianyl), 28.5 (s, CH<sub>2</sub> of 5-norbornyl), 30.6 (s, CH<sub>2</sub> of 6-norbornyl), 30.9 (s, CH<sub>2</sub> of 3-norbornyl), 35.2, 40.9 (s, CH<sub>2</sub> of 4,6-dithianyl), 45.1 (s, CH of 4-norbornyl), 50.5 (s, Cq of 7-norbornyl), 55.6 (s, Cq of 1-norbornyl), 114.5 (s, Cq of 2-norbornyl), 152.2 (s, Cq of 2-dithianyl)

MS (CI, NH<sub>3</sub>), m/z (relative intensity): 255 (M+1, 100)

*2-(Adamantan-2-ylidene)-1,3-dithiane (4j)*

Pale yellow oil crystallized in the cold, m.p. 45-46°C<sup>9a</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.60-2.20 (m, 14H, CH<sub>2</sub> of 4,6,8,9,10-adamantyl, CH of 5,7-adamantyl and CH<sub>2</sub> of 5-dithianyl), 2.75-2.90 (m, 4H, CH<sub>2</sub> of 4,6-dithianyl), 3.32 (br s, 2H, CH of 1,3-adamantyl)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  26.2 (s,  $\text{CH}_2$  of 5-dithianyl), 28.5 (s, CH of 5,7-adamantyl), 31.3 (s,  $\text{CH}_2$  of 10-adamantyl), 35.6 (s, CH of 1,3-adamantyl), 37.3 (s,  $\text{CH}_2$  of 4,6,8,9-adamantyl), 39.2 (s,  $\text{CH}_2$  of 4,6-dithianyl), 111.6 (s, Cq of 2-adamantyl), 154.2 (s, Cq of 2-dithianyl)

MS (CI,  $\text{NH}_3$ ), m/z (relative intensity): 253 (M+1, 100)

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