Thionation of Some α,β-Unsaturated Steroidal Ketones

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Abstract: The reactions of selected α,β-unsaturated steroidal ketones with Lawesson’s reagent (LR) in CH₂Cl₂ and toluene under the standard reaction conditions and with a combination of phosphorus pentasulfide with hexamethyldisiloxane (P₄S₁₀/HMDO) in 1,2-dichlorobenzene (ODCB) under microwave irradiation were investigated and for this purpose several cholestane, androstane and pregnane carbonyl derivatives were chosen. Depending on the reagent and the solvent, 19 new sulfur containing compounds, including dithiones 4c and 4d, α,β-unsaturated 3-thiones 3a-e, dimer-sulfides 2a-e, 1,2,4-trithiolanes 5a-e and phosphonotrithioates 6b-e were synthesized. All newly prepared compounds were characterized by IR, ¹H- and ¹³C-NMR spectroscopy and elemental analysis.

Keywords: α,β-unsaturated steroidal ketones; α,β-unsaturated 3-thiones; Lawesson’s reagent; P₄S₁₀/HMDO; dimerization, microwave irradiation

1. Introduction

Steroids are an important group of natural compounds possessing a variety of biological activities. The replacement of one or more carbon atoms in a steroid molecule by a heteroatom affects the chemical properties of that particular steroid and often results in alterations of its biological activity,
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which sometimes may be useful. Also, the addition of heterocyclic rings or new functional groups to steroid molecules often leads to changes in their physiological activity. Thionation is one possible modification that could have some influence on such activity. The larger and less electronegative sulfur atom, relative to oxygen, might alter the hydrogen-bonding ability and/or induce conformational changes in the modified molecule. In addition the increased reactivity of the thione function should make these derivatives useful intermediates for further transformations. Recently we reported synthesis of 6-thioxo-7-aza-B-homocholest-4-ene and 6-aza-7-thioxo-B-homocholest-4-ene using Lawesson’s reagent [1]. Continuing this investigation and our previous work on modified steroid compounds as biologically active molecules [1–4], the goal of this study was to synthesize some new thioxosteroid derivatives.

Several methods are reported in the literature for the thionation of organic compounds. Phosphorus pentasulfide (P$_4$S$_{10}$) was first reported in 1869 by Henry [5] and Wislicenus [6]. The usual procedure, which involves boiling toluene, xylene or pyridine as solvent, requires a large excess of reagent, long reaction time, and results in low and variable yields [7–9]. Recently Curphey [10–12] has shown that a combination of P$_4$S$_{10}$ with hexamethyldisiloxane (HMDO) efficiently converts esters, lactones, amides and ketones into their corresponding thio derivatives. Under the standard reaction conditions (dry toluene/xylene, thermal heating) this method has provided an increase in the selectivity and yield. Kaushik et al. developed a new thionating reagent by encapsulating the P$_4$S$_{10}$ in basic alumina [13]. The reactions were carried out in good to excellent yields by refluxing mixture of ketone and P$_4$S$_{10}$/Al$_2$O$_3$ in acetonitrile, but this method needs some more investigation. In 1978, Lawesson and coworkers developed a new reagent, 2,4-bis($p$-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide, commonly named Lawesson’s reagent (LR, Figure 1) [14–16].

![Figure 1. Lawesson’s reagent.](image)

The attractiveness of LR is associated with its commercial availability, simplicity and convenience of use, high yields and especially soft thionation reactions. In some cases the main disadvantage of this reagent is the formation of byproducts or stable heterocyclic intermediates. However, some of these sulfur and phosphorus containing products can be very useful as they have showed a promising antimicrobial and anti-inflammatory activity [17–20]. Since all described procedures require the use of dry aromatic hydrocarbon solvents and lengthy reaction times, microwave assistance has been applied to thionate a wide variety of substrates [21–25].

α,β-Unsaturated thiones are relatively little known, presumably due to their instability as monomeric species. Thus, the conversion of α,β-unsaturated ketones into corresponding thiones remains a challenging problem for organic chemists. Thionation of some steroidal ketones is already described in literature. Barton and coworkers synthesized several $\Delta^{1,4}$-diene-3-thioxo corticosteroids using P$_4$S$_{10}$ in pyridine as a reagent [26]. Weis et al. also described the regioselective thionation of 3-oxo-$\Delta^{1,4}$-diene steroid systems with LR in anhydrous THF [27]. Although several simple alicyclic
α,β-unsaturated thiones have been prepared, 3-thioxocholest-4-ene [28], 17-thioxoandrosta-4-en-3-one [19] and 3,17-dithioxoandrosta-4-ene [19] remain the only characterized steroidal examples. As far as we know there is no report dealing with the synthesis of thiono analogues of steroidal ketones under the microwave irradiation.

Herein we report on the reaction of several α,β-unsaturated cholestane, androstane and pregnane carbonyl derivatives 1a-e (Figure 2) with LR (in CH$_2$Cl$_2$ and toluene) under the standard reaction conditions and with a combination of P$_4$S$_{10}$/HMDO in 1,2-dichlorobenzene under microwave irradiation.

Figure 2. Substrates 1a-e.

2. Results and Discussion

The reactions of α,β-unsaturated ketones 1a-e with LR gave different products, depending on the solvent and duration of the reaction. Due to the instability of the unsaturated thioketones or dimers formed and their easy reconversion to the starting compounds a certain amount (8–52%) of the parent compounds was isolated in all cases.

At the beginning, the reaction procedure for thionation was carried out in refluxing toluene. Instantaneous reaction took place (the purple color of reaction mixture) with simultaneous formation of thionated products. Although there was no complete consumption of 1a-e, the reaction was quenched after 25–45 min (depending on substrate, see Experimental), while the solution was still purple, which was the evidence of the presence of thioketones. After flash column chromatography, besides corresponding dimer-sulfides 2a-e (7–56%), thioketones 3a-e were isolated in 11–27% yields (Scheme 1). When the reaction procedure was carried out in refluxing toluene for 8 h initially formed unstable α,β-unsaturated thioketones either dimerize to give corresponding dimer-sulfides 2a-e (30–51%), or decompose to a more stable starting ketones 1a-e (26–52%) (Scheme 1).
Scheme 1. Thionation of 1a-e with LR in toluene.

All obtained thioketones 3a-e were pink oils and their structures were determined on the basis of their spectral data (IR, $^1$H-NMR, $^{13}$C-NMR). In the IR spectra the absorption for the original unsaturated 3-oxo group, was missing, as well as the singlet for C-3 in the $^{13}$C-NMR spectra at about 199 ppm. Instead, the new singlet at $\delta$ 236.7, 237.0, 237.8, 236.9 and 237.4 ppm for C(3)=S, for compounds 3a-e, respectively, appeared. In the $^1$H-NMR spectra signal for H-4 at $\delta$ 6.63, 6.69, 6.74, 6.66 and 6.63 ppm was situated downfield comparing to the resonance for the corresponding proton in starting compounds 1a-e (at $\delta$ 5.72, 5.74, 5.84, 5.80 and 5.70 ppm, respectively). In addition, in all thioketones, both protons at C-2 ($\alpha$-position to the C=S group) resonate well-separated downfield from the other ring protons due to the strong C=S anisotropy, H-equatorial as a $td$ at about $\delta$ 3.15 ppm, H-axial as a $dt$ at about $\delta$ 2.50 ppm both with corresponding $J_{HH}$ coupling constants.

In the IR spectra of 2a-e the absorptions for the original unsaturated 3-oxo groups at 1667, 1665, 1667, 1665 and 1661 cm$^{-1}$ for 1a-e, respectively, were missing, as well as the singlet for C-3 in the $^{13}$C-NMR spectra at about $\delta$ 199 ppm. Instead, the new C-3 singlet at $\delta$ 129.4, 129.5, 129.5, 129.3, 129.4 ppm and the C-6 doublet at $\delta$ 124.3, 123.3, 124.8, 123.8 and 123.6 ppm for compounds 2a-e, respectively, appeared indicating the formation of a new double bond and $\Delta^{3,5}$-diene structure. New signal had also appeared in the $^1$H-NMR spectra: the broad triplet at $\delta$ 5.47, 5.45, 5.50, 5.42 and 5.39 ppm for H-6 for compounds 2a-e, respectively. On the other hand, the H-4 signal at $\delta$ 6.11, 6.13, 6.14, 6.11 and 6.10 ppm for compounds 2a-e, respectively, was shifted downfield comparing with that in starting compounds 1a-e (at $\delta$ 5.72, 5.74, 5.84, 5.80, 5.70 ppm, respectively). This can be explained by anisotropy effect of the new double bond in the dimers. On the basis of the COSY correlations between the vinylic H-6 and H$_2$-7 together with the key HMBC correlations from H-6 to C-7 and C-8.
the alternative $\Delta^{2,4}$-isomer was ruled out. Furthermore, the elemental analyses for 2a-e were in agreement with the proposed structures.

In order to increase the yield of thioketones we performed the same reactions under milder conditions, in CH$_2$Cl$_2$ as a solvent (refluxing for 45 min) and the thioketones 3a-e were obtained in much higher yield, 28–70%. Besides, steroids 1c-e gave corresponding 1,2,4-trithiolanes 5c-e. The steroids 1b and 1e gave also the (4-methoxy-phenyl)phosphonotrithioates 6b and 6e. In this reaction the formation of dithioketones 4c and 4d was observed as well and these products were also isolated but due to their instability we were able to record only IR spectra in which the absorption for the original unsaturated 3-oxo group was missing as well as the absorptions for carbonyls at C-17 for 4c and C-20 for 4d (Scheme 2).

Scheme 2. Thionation of 1a-e with LR in CH$_2$Cl$_2$. 

With a prolonged time of reaction in CH$_2$Cl$_2$ (reflux 4–8 h, depending on substrate, see Experimental) all unsaturated ketones 1a-e gave as a main product the corresponding 1,2,4-trithiolanes 5a-e (11–79%). Besides, steroids 1b-e gave also the (4-methoxyphenyl)phosphonotrithioates 6b-e.
(8–36%) as a result of further reaction of firstly formed thioketones with LR. In some cases (1a, 1c and 1d) the thioketones, 3a, 3c and 3d were still present in the reaction mixture and isolated in very poor yield (5–12%) (Scheme 2).

Support for the structures 5a-e was found from the \(^{13}\)C- and \(^1\)H-NMR spectral data as well as from the elemental analysis which showed that they contain three additional sulfur atoms (at two steroid molecules). NMR spectral data showed the absence of \(\alpha,\beta\)-unsaturated 3-oxo group. In the \(^1\)H-NMR spectra signal for H-4 at \(\delta\) 5.45, 5.44, 5.60, 5.47 and 5.46 ppm for 5a-e, respectively, was situated upfield comparing with that in the starting compounds 1a-e (at \(\delta\) 5.72, 5.74, 5.84, 5.80, 5.70 ppm, respectively), demonstrating the effect of an absence of the deshielding influence of 3-oxo group. In the \(^{13}\)C-NMR spectra the singlet for C-5 at \(\delta\) 152.5, 149.8 147.0, 151.9 and 151.8 ppm for 5a-e, respectively, was also situated upfield when compared to the corresponding resonance in 1a-e, indicated the absence of \(\alpha,\beta\)-unsaturated carbonyl group. In addition, the singlet for C-3 at about 199 ppm for starting compounds was missing and instead the new singlet at \(\delta\) 81.3, 80.2, 80.9, 81.1 and 81.1 ppm, respectively for 5a-e, appeared indicating the formation of 1,2,4-trithiolane ring.

In the IR spectra of phosphonotrithioates 6b-e the original C(3)=O absorption band disappeared, while in the \(^{13}\)C-NMR spectra the singlet for C-3 at about \(\delta\) 199 ppm was also absent. The \(^1\)H-NMR spectra showed the new olefinic H-6 proton signal, a broad triplet at \(\delta\) 5.52, 5.61, 5.49 and 5.47 ppm for 6b-e, respectively. On the other hand, the resonance for the olefinic H-4 proton appeared like two sets of signals, two doublets at \(\delta\) 6.30 and 6.34 ppm, 6.38 and 6.40 ppm, 6.28 and 6.32 ppm, 6.28 and 6.31 ppm for compounds 6b-e, respectively, with \(J_{PH}\) about 4 Hz indicated two different protons, both with the long range coupling with phosphorus. The signal for 19-Me group also appeared in pairs, two singlets at \(\delta\) 0.92 and 0.96 ppm for 6b, 0.89 and 0.92 ppm for 6d and 0.89 and 0.94 ppm for 6e. Besides, the new singlet at \(\delta\) 3.87, 3.86, 3.86 and 3.87 ppm (OCH\(_3\)) appeared as well as two doublets of doublets at \(\delta\) 6.96 and 8.02, 7.00 and 8.01, 6.96 and 8.02 and 6.95 and 8.01 ppm for aromatic protons for 6b-e, respectively, and these signals had corresponding \(J_{HH}\) and \(J_{PH}\) coupling constants. On basis of the peak areas ratio of the olefinic, methoxy and aromatic protons (H-4/H-6/OCH\(_3\)/ArH(3,5)/ArH(2,6)=2:2:3:2:2) it was deduced that two steroid molecules are attached with one monomeric species of LR to gave (4-methoxyphenyl)phosphonotrithioates 6b-e. The difference between H-4 protons and 19-methyl groups is attributed to the molecular asymmetry. This was confirmed by the \(^{13}\)C-NMR spectra in which the C-3 carbon atoms appeared like two doublets at \(\delta\) 124.5 and 124.8 ppm, 124.7 and 125.2 ppm, 124.4 and 124.5 ppm, 122.4 and 124.7 ppm for 6b-e, respectively, with \(2J_{PC}\) about 10 Hz. Furthermore, the signals for C-1, C-2, C-4, C-5, C-6, C-10 and 19-Me appeared like two sets of signals confirming proposed structures. Also, there were the signals for aromatic carbon atoms with corresponding \(1^4J_{PC}\) coupling constants at \(\delta\) 162.9, 133.7, 129.6 and 113.9 ppm for compound 6b, at \(\delta\) 162.9, 133.4, 129.6, 113.6 ppm for 6c, at \(\delta\) 162.6, 133.4, 128.1 and 113.6 ppm for 6d, and at \(\delta\) 162.6, 133.4, 127.7 and 113.6 ppm for 6e.

Thionation of steroidal ketones 1a-e with a combination of \(\text{P}_4\text{S}_{10}/\text{HMDO}\) under microwave irradiation in all cases gave two products: 3-thioketones 3a-e (11–26%) and dimer-sulfides 2a-e (7–42%). The yield of thioketones obtained was lower than in the reaction with LR in \(\text{CH}_2\text{Cl}_2\). In one case, in the reaction of 19-norandrost-4-ene-3,17-dione (1e) the 3,17-dithioketone 4c was isolated as well (3%) (Scheme 3).
Scheme 3. Thionation of 1a-e with P₄S₁₀/HMDO under the microwave irradiation.

3. Experimental Section

3.1. General

Removal of solvents was carried out under reduced pressure. Melting points were determined on an electrothermal capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer spectrophotometer FT-IR 1725X: \( \nu \) in cm\(^{-1}\). \(^1\)H- and \(^{13}\)C-NMR spectra were recorded on a Varian Gemini-200 spectrometer (at 200 and 50 MHz, respectively) and/or a Bruker Avance 500 MHz spectrometer (\(^1\)H at 500 MHz; \(^{13}\)C at 125 MHz) in CDCl\(_3\) and/or C\(_6\)D\(_6\) at room temperature using TMS as internal standard. Chemical shifts are expressed in ppm (\( \delta \)) values and coupling constants (\( J \)) in Hz. Mass spectra were taken on Finnigan-MAT 8230. Thin-layer chromatography was performed on precoated Merck silica gel 60 F\(_{254}\) plates in toluene/EtOAc (9:1, 8:2) and in \( n \)-hexane/EtOAc (8:2, 6:4), detection with 50% aq. H\(_2\)SO\(_4\) and/or with CAM solution. Flash column chromatography (FCC) was performed on silica gel Merck 0.040–0.063 mm under the Ar atmosphere. Elemental analyses were determined on Vario EL III. All starting steroid compounds were commercially available products.

3.2. General procedure for thionation with LR

LR (1 mmol) was added to a solution of steroidal ketone (1 mmol) in dichloromethane or toluene (15 mL). The reaction mixture was refluxed (duration mentioned in each experiment) with stirring and monitored by TLC. After the completion of reaction the rest of reagent was removed by filtration and
evaporated. The residue was chromatographed by FCC using toluene/EtOAc or n-hexane/EtOAc (ratio mentioned in each experiment) as eluent.

3.3. General procedure for thionation with combination of P₄S₁₀/HMDO under the microwave irradiation

All microwave assisted reactions were carried out using a modified Panasonic NN-S255W domestic microwave oven (2450 MHz, 800 W) which was adapted for laboratory applications with an external reflux condenser. The oven was perforated at the top for a condenser tube and external steel tube of the same diameter (~30 mm) was welded in order to eliminate possible microwave leakage.

P₄S₁₀ (0.5 mmol) was added to a solution of steroidal ketone (2 mmol) in ODCB (5 mL) placed in a 20 mL quartz vessel. The reaction mixture was stirred under the argon (Ar) for 10 minutes at room temperature and then HMDO (3.5 mmol) was added. The content was irradiated at 600 W for 90 seconds under Ar atmosphere with a pause of 2 min after every 20 seconds, monitored by TLC. After the completion of reaction the mixture was chromatographed by FCC using toluene/EtOAc or n-hexane/EtOAc (ratio mentioned in each experiment) as eluent.

3.3.1. Thionation of cholest-4-en-3-one (1a)

*In toluene 45 min:* Starting with 384 mg of 1a, elution with n-hexane gave dimer-sulfide 2a (216 mg, 56%). Oil. IR (CHCl₃): 2935, 1465, 732. ¹H-NMR (500 MHz, CDCl₃): 0.70 (s, 6H, 2×H₃C(18)), 0.86 and 0.87 (2d, 12H, 2×H₃C(26), 2×H₃C(27)), 0.92 (d, 6H, 2×H₃C(21)), 0.94 (s, 6H, 2×H₃C(19)), 5.41 (br.t, J = 4.5 Hz, 2H, 2×H-C(6)), 6.11 (2H, 2×H-C(4)). ¹³C-NMR (125 MHz): 141.6 (s, C(5)), 131.7 (d, C(4)), 129.4 (s, C(3)) 124.3 (d, C(6)), 56.9 (d, C(14)), 56.2 (d, C(17)), 48.1 (d, C(9)), 42.5 (s, C(13)), 39.8 (t, C(12)), 39.5 (t, C(24)), 36.2 (t, C(22)), 35.8 (d, C(20), 34.7 (s, C(10)), 34.7 (t, C(1)), 31.9 (t, C(7)), 31.8 (d, C(8)), 28.2 (t, C(16)), 28.0 (d, C(25)), 27.8 (t, C(2)), 24.2 (t, C(15)), 23.8 (t, C(23)), 22.8 (q, C(27)), 22.6 (q, C(26)), 21.1 (t, C(11)), 19.0 (q, C(19)), 18.7 (q, C(21)), 12.0 (q, C(18)). Anal. calcd for C₅₄H₈₆S: C 84.52; H 11.30; S 4.18. Found: C 84.07; H 11.56; S 4.28. Additionally starting material (70 mg, 18%) was recovered.

*In toluene 8 h:* Starting with 384 mg of 1a, elution with n-hexane gave dimer-sulfide 2a (112 mg, 30%) and starting material (200 mg, 52%).
In CH₂Cl₂ 45 min: Starting with 380 mg of 1a, elution with n-hexane gave dimer-sulfide 2a (95 mg, 25%). Further elution with n-hexane/toluene (70:30) gave 3-thioxocholest-4-ene (3a) (279 mg, 70%).

In CH₂Cl₂ 4h: Starting with 380 mg of 1a, elution with n-hexane and crystallization from MeOH gave 1,2,4-trithiolane 5a (330 mg, 79%). m.p. 134–136 ºC. IR (CHCl₃): 2929, 1464, 733. ¹H-NMR (200 MHz, CDCl₃): 0.67 (s, 6H, 2×H₃C(18)), 0.86 (d, 12H, 2×H₃C(26), 2×H₃C(27)), 0.93 (d, 6H, 2×H₃C(21)), 1.03 (s, 6H, 2×H₃C(19)), 5.45 (s, 2H, 2×H-C(4)). ¹³C-NMR: 152.5 (s, C(5)), 119.1 (d, C(4)), 81.3 (s, C(3)), 56.1 (d, C(17)), 55.9 (d, C(14)), 54.4 (d, C(9)), 42.4 (s, C(13)), 39.7 (t, C(12)), 39.5 (t, C(24)), 37.6 (s, C(10)), 37.3 (t, C(2)), 36.1 (t, C(22)), 35.8 (d, C(20)), 35.7 (d, C(8)), 35.0 (t, C(1)), 32.7 (t, C(7)), 32.4 (t, C(6)), 28.2 (t, C(16)), 28.0 (d, C(25)), 24.2 (t, C(15)), 23.8 (t, C(23)), 22.8 (q, C(27)), 22.5 (q, C(26)), 21.2 (t, C(11)), 18.6 (q, C(21)), 18.5 (q, C(19)), 11.9 (q, C(18)). Anal. calcd for C₅₄H₈₈S₃: C 77.82; H 10.61; S 11.54. Found: C 77.61; H 10.78; S 11.39. Further elution with n-hexane/toluene (70:30) gave 3-thioxocholest-4-ene (3a) (20 mg, 5%).

Under microwave irradiation: Starting with 762 mg of 1a, elution with n-hexane gave dimer-sulfide 2a (323 mg, 42%). Further elution with n-hexane/toluene (70:30) gave 3-thioxocholest-4-ene (3a) (153 mg, 19%). Starting material (244 mg, 32%) was also obtained.

3.3.2. Thionation of androst-4-ene-3,17-dione (1b)

In toluene 45 min: Starting with 860 mg of 1b, elution with toluene/EtOAc (97:3) and crystallization from MeOH gave dimer-sulfide 2b (182 mg, 21%). m.p. > 126 ºC (decomp.). IR (CHCl₃): 2940, 1737, 732. ¹H-NMR (200 MHz, CDCl₃): 0.91 (s, 6H, 2×H₃C(18)), 0.97 (s, 6H, 2×H₃C(19)), 5.45 (br. s, 2H, 2×H-C(6)), 6.13 (s, 2H, 2×H-C(4)). ¹³C-NMR: 221.1 (s, C(17)), 141.6 (s, C(5)), 131.4 (d, C(4)), 129.5 (s, C(3)), 123.3 (d, C(6)), 51.7 (d, C(14)), 48.0 (d, C(9)), 47.6 (s, C(13)), 35.7 (t, C(12)), 34.7 (s, C(10)), 34.5 (t, C(1)), 31.3 (t, C(7)), 31.3 (d, C(8)), 30.6 (t, C(16)), 27.6 (t, C(2)), 21.7 (t, C(15)), 20.3 (t, C(11)), 18.9 (q, C(19)), 13.6 (q, C(18)). Anal. calcd for C₃₈H₅₀O₂S: C 79.95; H 8.83; S 5.62. Found: C 79.80; H 9.06; S 5.70. Further elution with toluene/EtOAc (95:5) afforded 3-thioxoandrost-4-en-17-one (3b) (242 mg, 27%). Pink oil. IR (C₆D₆): 2936, 1735, 1579, 1010. ¹H NMR (200 MHz, C₆D₆): 0.63 (s, 3H, H₃C(18)), 0.74 (s, 3H, H₃C(19)), 2.52 (dd, J=17.6, 15.6, 5.0, 1H, Hβ-C(2)), 3.15 (dt, J=17.4, 3.4 Hz, 1H, Ha-C(2)), 6.69 (s, 1H, H-C(4)). ¹³C NMR (50 MHz, C₆D₆): 237.0 (s, C(3)), 217.7 (s, C(17)), 161.3 (s, C(5)), 135.4 (d, C(4)), 53.7 (d, C(9)), 50.6 (d, C(14)), 47.2 (s, C(13)), 43.5 (t, C(2)), 38.4 (s, C(10)), 36.5 (t, C(16)), 35.5 (t, C(6)), 34.9 (d, C(8)), 32.3 (t, C(7)), 31.7 (t, C(12)), 30.6 (t, C(1)), 21.6 (t, C(15)), 20.3 (t, C(11)), 16.7 (q, C(19)), 13.5 (q, C(18)). Starting material (69 mg, 8%) was also recovered.

In toluene 8h: Starting with 572 mg of 1b, elution with toluene/EtOAc (97:3) and crystallization from MeOH gave dimer-sulfide 2b (290 mg, 50%) and starting material (217 mg, 38%).

In CH₂Cl₂ 45 min: Starting with 572 mg of 1b, elution with toluene/EtOAc (97:3) gave dimer-sulfide 2b (27 mg, 5%). Further elution with toluene/EtOAc (95:5) afforded 3-thioxoandrost-4-en-17-one (3b) (197 mg, 33%). Elution with toluene/EtOAc (93:7) gave phosphonotrithioate 6b (27 mg, 4%). Starting material (228 mg, 40%) was also obtained.
In CH$_2$Cl$_2$ 8 h: Starting with 572 mg of 1b, elution with toluene/EtOAc (95:5) and crystallization from MeOH gave 1,2,4-trithiolane 5b (220 mg, 35%). m.p. 148–150 ºC. IR (CHCl$_3$): 2929, 1738, 1439, 732. $^1$H-NMR (200 MHz, CDCl$_3$): 0.87 (s, 6H, 2×H 3C(18)), 1.06 (s, 6H, 2×H 3C(19)), 5.44 (s, 2H, 2×H-C(4)). $^{13}$C-NMR: 220.9 (s, C(17)), 149.8 (s, C(5)), 119.2 (d, C(4)), 80.2 (s, C(3)), 53.9 (d, C(9)), 50.9 (d, C(14)), 47.6 (s, C(13)), 37.2 (s, C(10)), 39.7 (t, C(16)), 35.7 (t, C(1)), 35.2 (d, C(8)), 34.9 (t, C(2)), 32.2 (t, C(6)), 31.3 (t, C(7)), 29.6 (t, C(12)), 21.7 (t, C(15)), 20.4 (t, C(11)), 18.5 (q, C(19)), 13.69 (q, C(18)). Anal. calcd for C$_{38}$H$_{52}$O$_2$S$_3$: C 71.65, H 8.23, S 15.10. Found: C 71.19, H 8.27, S 14.84. Further elution with toluene/EtOAc (93:7) gave phosphonotrithioate 6b (280 mg, 36%). m.p. >133 ºC (decomp.). IR (CHCl$_3$): 2936, 1733, 1254, 1096, 828. $^1$H-NMR (500 MHz, CDCl$_3$): 0.89 and 0.90 (2s, 6H, 2×H3C(18)), 0.92 and 0.96 (2s, 6H, 2×H 3C(19)), 3.87 (s, 3H, OCH$_3$), 5.52 (br.s, 2H, 2×H-C(6)), 6.30 and 6.34 (2d, $^4$$J_{PH} = 3.0$ and 4.5 Hz, 2H, 2×H-C(4)), 6.96 (dd, $^4$$J_{PH} = 3.5$ Hz, J$_{HH} = 9.0$ Hz, 2H, 2×Ar-H). $^{13}$C-NMR (125 MHz): 220.2 (s, C(17)), 162.9 (sd, $^4$$J_{PC} = 2.9$ Hz, ArC-OCH$_3$), 142.08 and 141.05 (2sd, $^4$$J_{PC} = 3.6$ and 4.6 Hz, 2×C(5)), 141.46 and 141.38 (2dd, both $^3$$J_{PC} = 5.5$ Hz, 2×C(4)), 133.7 (dd, $^3$$J_{PC} = 12.5$ Hz, 2×ArC-H), 129.6 (sd, $^3$$J_{PC} = 91.8$ Hz, ArC-P), 126.83 and 126.80 (2d, 2×C(6)), 124.7 and 124.5 (2sd, $^2$$J_{PC} = 12.8$ and 9.1, 2×C(3)), 113.9 (dd, $^2$$J_{PC} = 15.0$, 2×ArC-H), 55.7 (q, OCH$_3$), 52.0 (d, C(14)), 48.2 (d, C(9)), 47.9 (s, C(13)), 36.0 (t, C(16)), 35.0 and 34.9 (2t, 2×C(1)), 34.73 and 34.70 (2s, 2×C(10)), 31.6 (d, C(7)), 31.5 (t, C(8)), 31.4 and 31.2, 2t, 2×C(2)), 31.06 (t, C(12)), 22.0 (t, C(15)), 20.6 (t, C(11)), 19.16 and 19.22 (2q, 2×C(19)), 13.9 (q, C(18)). ESI-TOF-MS: m/z calcd for C$_{45}$H$_{57}$O$_3$PS$_3$: 773.3286 [M+H]$^+$, found 773.2404. Starting material (46 mg, 8%) was recovered too.

Under microwave irradiation: Starting with 572 mg of 1b, elution with toluene/EtOAc (93:7) gave dimer-sulfide 2b (105 mg, 19%). Further elution with toluene/EtOAc (95:5) afforded 3-thioxoandrost-4-en-17-one (3b) (100 mg, 17%). Starting material (195 mg, 34%) was isolated.

3.3.3. Thionation of 19-norandrost-4-ene-3,17-dione (1c)

In toluene 25 min: Starting with 540 mg of 1c, elution with toluene/EtOAc (98:2) afforded dimer-sulfide 2c (37 mg, 7%). IR (CHCl$_3$): 2928, 1737. $^1$H-NMR (200 MHz, CDCl$_3$): 0.92 (s, 6H, 2×H$_2$C(18)), 5.55 (br. s, 2H, 2×H-C(6)), 6.14 (s, 2H, 2×H-C(4)). $^{13}$C-NMR: 221.01 (s, C(17)), 141.6 (s, C(5)), 131.4 (d, C(4)), 129.5 (s, C(3)), 124.8 (d, C(6)), 50.1 (d, C(14)), 49.4 (d, C(9)), 47.7 (s, C(13)), 42.4 (s, C(10)), 42.4 (d, C(8)), 36.4 (t, C(16)), 31.3 (t, C(7)), 30.6 (t, C(12)), 29.6 (t, C(2)), 26.5 (t, C(1)), 25.6 (t, C(11)), 21.7 (t, C(15)), 13.6 (q, C(18)). Anal. calcd for C$_{36}$H$_{36}$O$_2$S: C 79.66; H 8.54; S 5.91. Found: C 79.80; H 8.72; S 6.00. Further elution with toluene/EtOAc (97:3) afforded 3-thioxo-19-norandrost-4-en-17-one (3c) (140 mg, 25%). Pink oil. IR (C$_6$D$_6$): 2929, 1731, 1560, 1034. $^1$H-NMR (500 MHz, C$_6$D$_6$): 0.60 (s, 3H, H$_3$C(18)), 2.35 (dd, J = 15.8, 14.5, 4.5 Hz, 1H, Hβ-C(2)), 3.15 (dt, J = 16.5, 4.0 Hz, 1H, Hα-C(2)), 6.75 (s, 1H, H-C(4)). $^{13}$C-NMR (125 MHz, C$_6$D$_6$): 237.8 (s, C(3)), 217.8 (s, C(17)), 156.9 (s, C(5)), 136.6 (d, C(4)), 50.3 (d, C(14)), 49.7 (d, C(9)), 47.7 (s, C(13)), 46.5 (t, C(2)), 42.9 (d, C(10)), 40.1 (d, C(8)), 35.9 (t, C(16)), 35.4 (t, C(6)), 32.1(t, C(7)), 30.2 (t, C(12)), 27.9 (t, C(1)), 26.0 (t, C(15)), 21.9 (t, C(11)), 14.0 (q, C(18)). Anal. calcd for C$_{18}$H$_{24}$O$_2$S: C 74.95; H 8.39; S 11.27. Found: C 75.10; H 8.68; S 11.27. Starting material (200 mg, 37%) was isolated.
In toluene 8 h: Starting with 540 mg of 1c, elution with toluene/EtOAc (98:2) afforded dimer-sulfide 2c (230 mg, 43%) and starting material (140 mg, 26%).

In CH₂Cl₂ 45 min: Starting with 544 mg of 1c, elution with toluene/EtOAc (99:1) gave 3,17-dithioxo-19-norandrost-4-ene (4c) (29 mg, 5%). IR (KBr): 2845, 1582. Further elution with toluene/EtOAc (97:3) afforded 3-thioxo-19-norandrost-4-en-17-one (3c) (220 mg, 38%). Further elution with toluene/EtOAc (95:5) gave 1,2,4-trithiolane 5c (99 mg, 16%). IR (CHCl₃): 2928, 1737, 1403. Further elution with toluene/EtOAc (97:3) afforded 3-thioxo-19-norandrost-4-en-17-one (3c) (220 mg, 38%). Further elution with toluene/EtOAc (95:5) gave 1,2,4-trithiolane 5c (99 mg, 16%). IR (CHCl₃): 2928, 1737, 1403. 

In CH₂Cl₂ 7 h: Starting with 544 mg of 1c, elution with toluene/EtOAc (97:3) afforded 3-thioxo-19-norandrost-4-en-17-one (3c) (47 mg, 8%). Further elution with toluene/EtOAc (95:5) gave 1,2,4-trithiolane 5c (65 mg, 11%). Further elution with toluene/EtOAc (94:6) gave phosphonotrithioate 6c (59 mg, 8%). Further elution with toluene/EtOAc (99:1) gave 3,17-dithioxo-19-norandrost-4-ene (4c) (18 mg, 3%). IR: 2845, 1582, 1035. Further elution with toluene/EtOAc (98:2) afforded dimer-sulfide 2c (38 mg, 7%). Further elution with toluene/EtOAc (97:3) afforded 3-thioxo-19-norandrost-4-en-17-one (3c) (149 mg, 26%). Starting material (86 mg, 16%) was isolated.

3.3.4. Thionation of progesterone (1d)

In toluene 45 min: Starting with 314 mg of 1d, elution with toluene/EtOAc (99:1) gave 3,17-dithioxo-19-norandrost-4-ene (4c) (18 mg, 3%). IR: 2845, 1582, 1035. Further elution with toluene/EtOAc (98:2) afforded dimer-sulfide 2c (38 mg, 7%). Further elution with toluene/EtOAc (97:3) afforded 3-thioxo-19-norandrost-4-en-17-one (3c) (149 mg, 26%). Starting material (86 mg, 16%) was isolated.
In toluene 8 h: Starting with 314 mg of \(1d\), elution with toluene/EtOAc (98:2) gave dimer-sulfide \(2d\) (160 mg, 51%) and starting material (106 mg, 34%).

In \(\text{CH}_2\text{Cl}_2\) 45 min: Starting with 630 mg of \(1d\), elution with toluene/EtOAc (99:1) gave 3,20-dithioxoprogesterone (\(4d\)) (66 mg, 9%). IR (KBr): 2939, 1576, 1010. Further elution with toluene/EtOAc (98:2) afforded 3-thioxoprogesterone (\(3d\)) (185 mg, 28%). Further elution with toluene/EtOAc (97:3) gave \(1,2,4\)-trithiolane \(5d\) (114 mg, 16%). IR (CHCl3): 2934, 1702, 1492. \(^1\)H-NMR \((200 \text{ MHz, CDCl}_3\)): 0.63 (s, 6H, \(2 \times \text{H}_3\text{C}(18)\)), 1.03 (s, 6H, \(2 \times \text{H}_3\text{C}(19)\)), 2.13 (s, 6H, \(2 \times \text{H}_3\text{C}(21)\)), 5.47 (s, 2H, \(2 \times \text{H}-\text{C}(4)\)). \(^13\)C-NMR: 209.5 (s, C(20)), 151.9 (s, C(5)), 119.3 (d, C(4)), 81.1 (s, C(3)), 63.5 (d, C(17)), 54.2 (d, C(9)), 44.0 (s, C(13)), 38.7 (t, C(12)), 37.2 (s, C(10)), 37.2 (t, C(2)), 35.6 (d, C(8)), 34.9 (t, C(1)), 32.5 (t, C(6)), 32.1 (t, C(7)), 31.4 (q, C(21)), 24.3 (t, C(15)), 22.7 (t, C(16)), 21.1 (t, C(11)), 16.5 (q, C(19)), 13.2 (q, C(18)). Anal. calcd for \(\text{C}_{42}\text{H}_{60}\text{O}_2\text{S}_3\): C 72.78; H 8.73; S 13.88. Found: C 72.91; H 8.67; S 13.80. Recovered starting material: 176 mg (28%).

In \(\text{CH}_2\text{Cl}_2\) 7 h: Starting with 630 mg of \(1d\), elution with toluene/EtOAc (99:1) gave 3-thioxoprogesterone (\(3d\)) (78 mg, 12%). Further elution with toluene/EtOAc (97:3) gave 1,2,4-trithiolane \(5d\) (185 mg, 27%). Further elution with toluene/EtOAc (96:4) gave phosphonotrithioate \(6d\) (110 mg, 13%). IR (CHCl3): 2936, 1702, 1257, 1098, 830. \(^1\)H-NMR \((500 \text{ MHz, CDCl}_3\)): 0.63 and 0.640 (2s, 6H, \(2 \times \text{H}_3\text{C}(18)\)), 0.89 and 0.92 (2s, 6H, \(2 \times \text{H}_3\text{C}(19)\)), 2.117 and 2.120 (2s, 6H, \(2 \times \text{H}_3\text{C}(21)\)), 3.86 (s, 3H, OCH\(_3\)), 5.49 (br.s, 2H, \(2 \times \text{H}-\text{C}(6)\)), 6.28 and 6.32 (2d, \(^4\)J\(_{\text{PH}}\) = 4.5 and 6.0 Hz, 2H, \(2 \times \text{H}-\text{C}(4)\)), 6.96 (dd, \(^4\)J\(_{\text{PH}}\) = 3.2 Hz, \(J_{\text{HH}} = 9.0 \text{ Hz}, 2 \times \text{Ar-H}\)), 8.02 (dd, \(^3\)J\(_{\text{PH}}\) = 14.0 Hz, \(J_{\text{HH}} = 9.0 \text{ Hz}, 2 \times \text{Ar-H}\)). \(^{13}\)C NMR \((125 \text{ MHz})\): 209.4 (s, C(20)), 162.6 (sd, \(^4\)J\(_{\text{PC}}\) = 2.9 Hz, ArC-OCH\(_3\)), 141.6 and 141.7 (2sd, \(^2\)J\(_{\text{PC}}\) = 3.7 Hz, 2 \times \(\text{C}(5)\)), 141.27 and 141.35 (2dd, \(^3\)J\(_{\text{PC}}\) = 5.5 Hz, 2 \times \(\text{C}(4)\)), 133.4 (dd, \(^3\)J\(_{\text{PC}}\) = 12.8 Hz, 2 \times \(\text{Ar-C-H}\)), 128.1 (sd, \(\text{J}_{\text{PC}}\) = 84.6 Hz, Ar-C-P), 127.23 and 127.20 (2dd, \(^5\)J\(_{\text{PC}}\) = 3.7 and 5.0 Hz, 2 \times \(\text{C}(6)\)), 124.5 and 124.4 (2sd, \(^2\)J\(_{\text{PC}}\) = 8.7 and 10.0 Hz, 2 \times \(\text{C}(3)\)), 113.6 (d, \(^2\)J\(_{\text{PC}}\) = 15.0 Hz, 2 \times \(\text{Ar-C-H}\)), 63.5 (d, C(17)), 56.9 (d, C(9)), 55.5 (q, OCH\(_3\)), 47.7 (d, C(14)), 44.1 (s, C(13)), 38.7 (t, C(12)), 34.80 and 34.78 (2t, \(2 \times \text{C}(1)\)), 34.34 and 34.31 (2s, \(2 \times \text{C}(10)\)), 31.8 (t, C(7)), 31.6 (d, C(8)), 31.5 (q, C(21)), 31.3 and 31.1 (2t, \(2 \times \text{C}(2)\)), 24.2 (t, C(15)), 20.9 (t, C(11)), 18.93 and 18.88 (2q, \(2 \times \text{C}(19)\)), 13.3 (q, C(18)). ESI-TOF-MS: \(m/z\) calcd for \(\text{C}_{49}\text{H}_{65}\text{O}_3\text{PS}_3\): 829.39062 [M+H]\(^+\), found 829.38920. In addition starting material (120 mg, 19%) was isolated.

Under microwave irradiation: Starting with 630 mg of \(1d\), elution with toluene/EtOAc (99:1) gave 3-thioxoprogesterone (\(3d\)) (72 mg, 11%). Further elution with toluene/EtOAc (98:2) afforded dimer-sulfide \(2d\) (152 mg, 25%). Starting material (158 mg, 28%) was also recovered.
3.3.5. Thionation of 16α,17α-epoxyprogesterone (1e)

**In toluene 25 min:** Starting with 500 mg of 1e, elution with toluene/EtOAc (99:1) gave 3-thioxo-16α,17α-epoxyprogesterone (3e) (105 mg, 20%). Pink oil. IR (C6D6): 2942, 1701, 1574, 1075. 
1H-NMR (500 MHz, C6D6): 0.67 (s, 3H, H3C(18)), 0.98 (s, 3H, H3C(19)), 1.77 (s, 3H, H3C(21)), 2.44 (ddt, J = 16.2, 15.8, 5.0 Hz, 1H, Hβ-C(2)), 3.04 (s, H-C(16)), 3.09 (dt, J = 17.5, 3.5 Hz, 1H, Hα-C(2)), 6.63 (s, 1H, H-C(4)). 
13C-NMR (125 MHz, C6D6): 237.4 (s, C(3)), 204.0 (s, C(20)), 161.3 (s, C(5)), 135.8 (d, C(4)), 71.1 (s, C(17)), 54.1 (d, C(9)), 45.4 (d, C(14)), 43.9 (t, C(2)), 42.1 (s, C(13)), 38.8 (t, C(12)), 38.8 (s, C(10)), 33.6 (d, C(8)), 32.8 (t, C(6)), 31.9 (t, C(7)), 31.8 (t, C(1)), 27.7 (t, C(15)), 25.9 (q, C(21)), 21.8 (t, C(11)), 17.0 (q, C(19)), 15.7 (q, C(18)).

Further elution with toluene/EtOAc (98:2) afforded gave dimer-sulfide 2e (122 mg, 25%). IR (CHCl3): 2939, 1703, 1376. 
1H-NMR (200 MHz, CDCl3): 0.95 (s, 6H, 2×H3C(19)), 1.06 (s, 6H, 2×H3C(18)), 2.02 (s, 6H, 2×H3C(21)), 3.68 (s, 2H, 2×H-C(16)), 5.39 (br. s, 2H, 2×H-C(6)), 6.10 (s, 2H, 2×H-C(4)). 
13C-NMR (50 MHz, CDCl3): 204.8 (s, C(20)), 141.6 (s, C(5)), 131.4 (d, C(4)), 129.4 (s, C(3)), 123.3 (d, C(6)), 70.8 (s, C(17)), 60.3 (d, C(16)), 48.1 (d, C(14)), 45.4 (d, C(9)), 41.5 (s, C(13)), 34.7 (s, C(10)), 34.4 (t, C(1)), 31.2 (t, C(12)), 31.1 (t, C(2)), 29.4 (d, C(8)), 27.2 (t, C(15)), 25.8 (q, C(21)), 21.3 (t, C(11)), 18.8 (q, C(19)), 15.1 (q, C(18)).

Anal. calcd for C42H54O4S: C 77.02; H 8.31; S 4.90. Found: C 77.38; H 8.53; S 5.10. Starting material recovered: 180 mg (36%).

**In toluene 8 h:** Starting with 500 mg of 1e, elution with toluene/EtOAc (98:2) afforded gave dimer-sulfide 2e (202 mg, 41%) and starting material (155 mg, 31%).

**In CH2Cl2 45 min:** Starting with 500 mg of 1e, elution with toluene/EtOAc (99:1) gave 3-thioxo-16α,17α-epoxyprogesterone (3e) (185 mg, 35%). Further elution with toluene/EtOAc (98:2) and crystallization from CH3OH afforded 1,2,4-trithiolane 5e (62 mg, 6%). m.p. > 147 ºC (decomp.). IR (CHCl3): 2936, 1705, 1377, 733. 
1H-NMR (200 MHz, CDCl3): 1.03 (s, 6H, 2×H3C(19)), 1.04 (s, 6H, 2×H3C(18)), 2.02 (s, 6H, 2×H3C(21)), 3.66 (s, 2H, 2×H-C(16)), 5.46 (s, 2H, 2×H-C(4)). 
13C-NMR (50 MHz, CDCl3): 204.9 (s, C(20)), 151.8 (s, C(5)), 81.1 (s, C(3)), 70.8 (s, C(17)), 60.4 (d, C(16)), 54.5 (d, C(9)), 44.8 (d, C(14)), 41.6 (s, C(13)), 37.3 (t, C(2)), 37.3 (s, C(10)), 34.9 (t, C(1)), 33.3 (d, C(8)), 32.2 (t, C(6)), 32.2 (t, C(7)), 31.2 (t, C(12)), 27.3 (t, C(15)), 25.9 (q, C(21)), 20.5 (t, C(11)), 18.3 (q, C(19)), 15.2 (q, C(18)).

Anal. calcd for C42H56O4S3: C 69.96; H 7.83; S 13.34. Found: C 69.68; H 8.11; S 13.47. Further elution with same eluent gave phosphonotrithioate 6e (42 mg, 7%).

Oil. IR (CHCl3): 2941, 1701, 1135, 984, 723. 
1H-NMR (200 MHz, CDCl3): 0.89 and 0.94 (2s, 6H, 2×H3C(19)), 1.05 (s, 6H, 2×H3C(18)), 2.02 (s, 6H, 2×H3C(21)), 3.69 (s, 2H, 2×H-C(16)), 3.87 (s, 3H, OCH3), 5.47 (br. s, 2H, 2×H-C(6)), 6.28 and 6.31 (2sd, JPH = 5.8 and 6.0 Hz, 2H, 2×H-C(4)), 6.95 (dd, JPH = 3.0 Hz, JHH = 8.8 Hz, 2H, 2×Ar-H), 8.01 (dd, JPH = 14.0 Hz, JHH = 8.8 Hz, 2H, 2×Ar-H). 
13C-NMR (50MHz, CDCl3): 204.8 (s, C(20)), 162.6 (s, Ar-C-OCH3), 141.85 and 141.78 (2s, C(5)), 141.3 and 141.1 (2d, 2×C(4)), 133.4 (dd, JPC = 12.8 Hz, 2×Ar-C-H), 127.7 (sd, JPC = 84.7 Hz, Ar-C-P), 126.7 (d, C(6)), 124.7 and 124.4 (2sd, both JPC = 9.1 Hz, 2×C(3)), 113.6 (dd, JPC=14.6, 2×Ar-C-H), 70.8 (s, C(17)), 60.3 (d, C(16)), 55.4 (q, OCH3), 47.9 (d, C(9)), 45.4 (d, C(14)), 41.5 (s, C(13)), 34.6 (t, C(1)), 34.4 (s, C(10)), 31.4 (t, C(12)), 31.2 (t, C(7)), 31.0 (t, C(2)), 29.3 (d, C(8)), 27.3 (t, C(15)), 25.8 (q, C(21)), 20.3 (t, C(11)), 18.8 (q, C(19)), 15.1 (q, C(18)). Starting material obtained: 135 mg (27%).
In CH$_2$Cl$_2$ 8h: Starting with 500 mg of 1e, elution with toluene/EtOAc (98:2) gave 1,2,4-trithiolane 5e (200 mg, 36%). Further elution with same eluent gave phosphonotrithioate 6e (180 mg, 28%). Starting material: 50 mg (10%).

Under microwave irradiation: Starting with 500 mg of 1e, elution with toluene/EtOAc (99:1) gave 3-thioxo-16a,17a-epoxyprogesterone (3e) (63 mg, 12%). Further elution with toluene/EtOAc (98:2) afforded dimer-sulfide 2e (127 mg, 26%). Starting material isolated: 120 mg (24%).

4. Conclusions

In this work we showed that Lawesson’s reagent can be suitable for preparation of α,β-unsaturated steroidal thioketones as well as different, depending on the solvent, sulfur steroid derivatives. α,β-Unsaturated ketones 1a-e in boiling toluene gave, besides dimer-sulfides 2a-e, the thioketones 3a-e in 11–27% yields. Much higher yields of thioketones were obtained when thionation was carried out in CH$_2$Cl$_2$ (28–70%). In this reaction the dithioketones 4c and 4d were isolated as well. With prolonged reaction times in both solvents and due to the enethiones instability and formation of by-products neither thioketone could be isolated. In toluene, the initially formed unstable enethiones dimerize to give only the corresponding dimer-sulfides 2a-e (30–51%). In CH$_2$Cl$_2$ all unsaturated ketones 1a-e gave as a main product the corresponding dimers with 1,2,4-trithiolane ring 5a-e in 11-79% yields, and (4-methoxyphenyl)phosphonotrithioates 6b-e (8–36%) as a result of further reaction of the initially formed thioketones with LR.

The combination of P$_4$S$_{10}$/HMDO under the microwave irradiation can also be applied for thionation of α,β-unsaturated steroids. This reaction gave two main products, 3-thioketones 3a-e and dimer-sulfides 2a-e. However, the yields of synthesized thioketones (11–26%) were lower than in the reaction with LR.

Although all obtained products were separated using flash column chromatography partial decomposition to the more stable starting α,β-unsaturated ketones took place in all cases. The synthetic results of this work could be useful for chemists in general, not only those working in the field of steroid chemistry. It could be used for preparation of α,β-unsaturated thioketones as well as new sulfur and/or phosphorus containing compounds.

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*Sample Availability:* Samples of the compounds are available from the authors.

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