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Synthesis of Enol Methyl Ethers of 3-Acetyl-6,6-dimethyltetrahydrothiopyran-2,4-dione and Their Reactions with Amines

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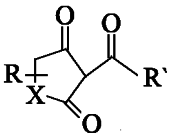
Abstract—The reaction of 3-acetyl-6,6-dimethyltetrahydrothiopyran-2,4-dione with diazomethane furnishes a mixture of 3-acetyl-6,6-dimethyl-4-methoxy-5,6-dihydro-2*H*-thiopyran-2-one and 3-acetyl-6,6-dimethyl-2-methoxy-5,6-dihydro-2H-thiopyran-4-one in 2 : 3 ratio, whereas in reaction with dimethyl sulfate in the presence of potassium carbonate forms a mixture of the same products in 9 : 1 ratio. In both reactions the overall yield of ethers amounts to 50%. Treating of regioisomeric enol methyl ethers with pyrrolidine, *o*-toluidine, and allylamine provides the corresponding endocyclic enaminodiketones.

Versatile biological properties [1] and a rich synthetic potential [2] of polyfunctional β-tricarbonyl moiety attract a strong interest to the cyclic β-triketones **Ia–f** of researchers working in the field of synthesis of natural substances and their biologically active analogs. At present among the heterocyclic β-triketones are well studied naturally occurring 3-acylated tetronic (**Ic**) and tetramic (**Id**) acids [4]. Sulfur-containing heterocyclic β-tricarbonyl compounds **Ie, If** are less understood. We showed before that 3-acylthiotetronic acids **Ie** can be used in the synthesis of N,S-diheteroanalogs of steroids [5]. In the course of these investigations we advanced new synthetic methods both for 3-acylthiotetronic acids proper and for their various derivatives [6].



Ia–e

X = CH_2 (**a**), CH_2CH_2 (**b**), O (**c**), N (**d**), S (**e**), CH_2S (**f**; R,R' = alkyl, aryl, alkylaryl.

When we turned our attention to β-triketones of the thiopyran series **If** we found that only scanty publication appeared concerning synthesis and chemical reactions of thiopyran-2,4-diones derivatives [7, 8]. Bactericidal and fungicidal properties were described of brominated derivatives of 3-acetyl-2*H*-thiopyran-2,4(3*H*)-dione [4]. As herbicides were patented derivatives of 3-acyl-2*H*-thiopyran-2,4(3*H*)-diones (**If**) [10–14]. We did not find any publications on the synthesis of enol methyl ethers and enamino derivatives of thiopyran β-triketones.

As the most general approach to building up of thiopyran-2,4-dione ring should be regarded the condensation of α,β-unsaturated ketones with dialkylammonium *N,N*-dialkyldithiocarbamates that arise on treating secondary amines with hydrogen sulfide [7]. By reaction of mesityl oxide (**II**) with pyrrolidinium dithiocarbamate (**III**) followed by oxidation of condensation product **IV** with alkaline hydrogen peroxide into enaminoketone **V** and acid hydrolysis of the latter along the procedures described in [7] was obtained in overall yield 50% the target 6,6-dimethyltetrahydrothiopyran-2,4-dione (**VI**). Physicochemical characteristics both of the target and intermediate compounds were consistent with the published data [7].

In order to have a possibility of the proper assignment of the methylene protons signals in the ^{1}H NMR spectra of regioisomers we also prepared enamino derivative at the C^2-carbonyl group, enaminoketone **IX**. To this end pyrrolidine enamine **IV** was treated in benzene with dimethyl sulfate, then salt **VII** obtained was hydrolyzed to thioether **VIII** that under mild conditions reacted with pyrrolidine to afford enaminoketone **IX** in an overall yield 76–80%. The reaction of regioisomeric enaminoketones **V** and **IX** with acetyl chloride in the presence of 4-dimethylaminopyridine (DMAP) provided the 3-acyl derivatives of the corresponding 2- and 4-enamines **X** and **XI**.

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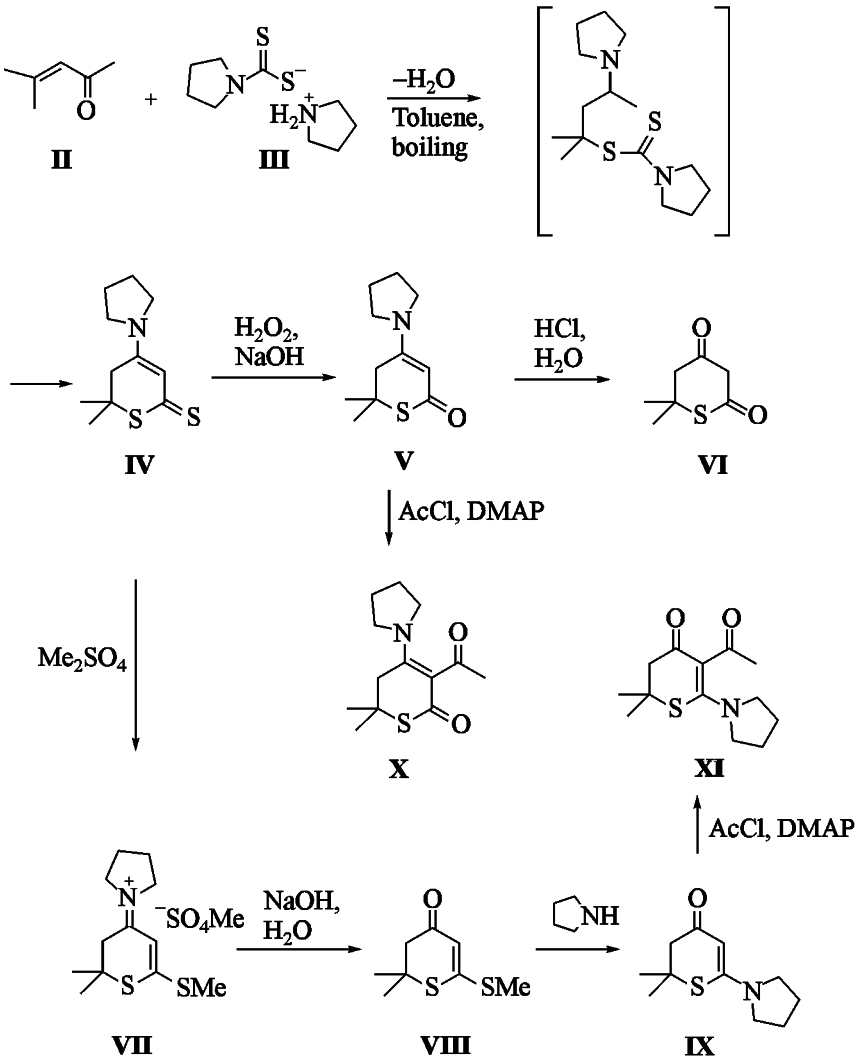
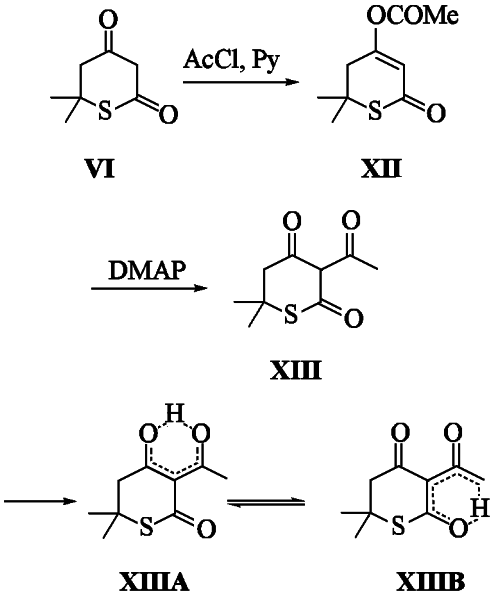


The analysis of ^{1}H NMR spectra of these pyrrolidine enamines **V, IX–XI** showed that the rules observed in the chemical shifts of the methylene protons signals corresponding to the ring of derivatives of (3*H*,5*H*)tetrahydrothiophene-2,4-dione (thiotetronic acid) [6, 14] are also valid for the spectra of derivatives of tetrahydrothiopyran-2,4-dione. In the ^{1}H NMR spectra of the compounds under study appear all the proton signals in the regions appropriate for their chemical surrounding. Therewith the signals of methylene protons attached to C^5 and adjacent to the enamine moiety appear downfield with respect to the signals of C^5-methylene protons neighboring to the carbonyl group, namely, at 2.52 ppm in compound **V** and 2.60 ppm in compound **IX**, at 2.61 ppm in compound **X** and 2.92 ppm in compound **XI**. This downfield shift can serve a criterion for compounds of this series of double bond position either at *2* or *3*.

In contrast to thiotetronic acid that gave on acylation a mixture of O-acyl esters at both carbonyl groups [6], thiopyran-2,4-dione (**VI**) treated with acetyl chloride in toluene in the presence of pyridine furnished a single O-acetyl derivative. As suggested the position in the ^{1}H NMR spectrum of the singlet of methylene protons attached to C^5 that appeared at 2.80 ppm we obtained enol ester at the C^4-oxo group of the dicarbonyl system **XII** in agreement with the published data [11]. The obtained enol acylate **XII** under treatment with dimethylaminopyridine underwent isomerization into thiopyran β-triketone **XIII** that was isolated in 66% yield.

According to ^{1}H NMR data triketone **XIII** is completely enolized and exists as an intramolecular chelate. The latter fact is evidenced by a signal of enol proton at 18.4 ppm. Usually in the ^{1}H NMR spectrum of unsymmetrical β-triketones is observed a double



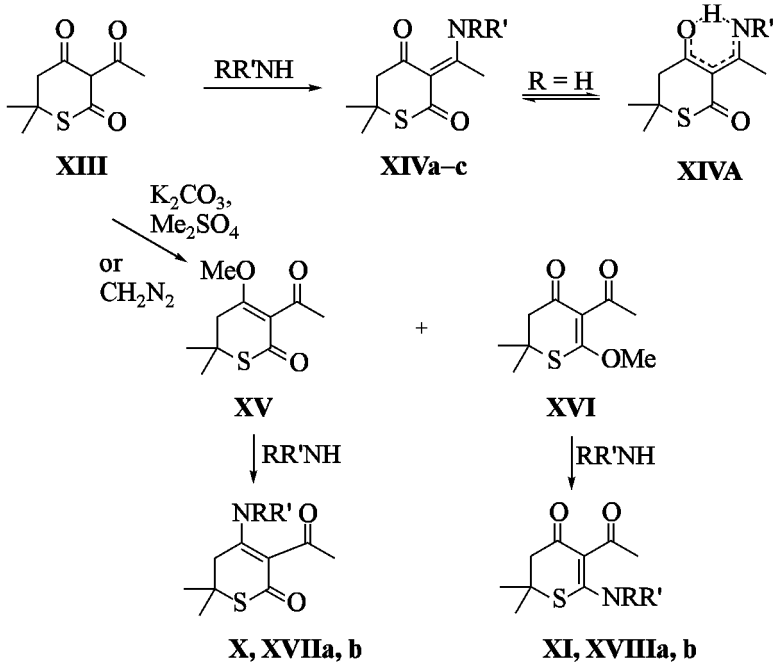
VI **XII** **XIII** **XIIIA** **XIIIB**

set of signals from proton-containing groups corresponding to two directions of enolization and consequently to two tautomeric forms **A** and **B** [2, 6]. The ^{1}H NMR spectrum of triketone **XIII** does not possess a double set of signals, i.e., compound **XIII** exists in a single enol form. Since the methylene protons at C^5 in the thiopyran ring give a singlet signal at 2.96 ppm. in keeping with the above stated criterion this triketone exists in **A** form.

Reaction of triketone **XIII** with pyrrolidine, allylamine, and o-toluidine takes the same route as with 3-acetylthiotetronic acid [6] and the other cyclic β-triketones: It occurs at the carbonyl group of the side acyl chain giving rise to enaminodiketones **XIVa–c** in 72–88% yield. The structure of enamino derivatives **XIVa–c** is proved by the combination of data of elemental analysis, ^{1}H NMR, IR, and mass spectra.

It should be noted that unlike the enamino derivatives of thiotetronic acid the enaminodiketones **XIVa–c** according to a single set of proton signals in their ^{1}H NMR spectra apparently exist in solution in a single tautomeric form: Since the singlet of the methylene protons at C^5 appears at about 2.80 ppm they take most likely the structure **XIVA**.

It is known [2] that involving into the reaction with amines of enol methyl ethers of the β-triketones it is possible to change the direction of the nucleophile attack and to obtain as a result of vinyl substitution enamino derivatives at the carbonyl group in the ring. Attempting to prepare enol methyl ethers of 3-acetyltetrahydrothiopyran-1,4-dione we studied reaction of its potassium salts with dimethyl sulfate in benzene, and also its reaction with ethereal solution of diazo-



XIII **XIVa–c** **XIVA** **XV** **XVI** **X, XVIIa, b** **XI, XVIIIa, b**

XIV, RR' = $(CH_2)_4$ (a); R = H, R' = *o*-MeC_6H_4 (**b**); R = H, R' = $CH_2CH{=}CH_2$ (**c**); **XVII**–**XVIII**, R = H, R' = *o*-MeC_6H_4 (**a**); R = H, R' = $CH_2CH{=}CH_2$ (**b**).

methane. Treating with any of the reagents provided mixtures of regioisomeric 4-methoxy (**XV**) and 2-methoxy (**XVI**) derivatives in 50–55% yield.

However if at application of diazomethane the ratio of methyl ethers **XV** and **XVI** was 2 : 3, the alkylation with dimethyl sulfate unexpectedly yielded the same ethers in 9 : 1 ratio. This is the first example of a cyclic tricarbonyl system where the direction of its salts alkylation is opposite to the direction of enolization. In the ^{1}H NMR spectra of ethers **XV** and **XVI** the enol proton signal at 18.4 ppm characteristic of the initial β-triketone is lacking, and appear tree-proton singlets of methoxy groups protons at 3.94 and 3.95 ppm respectively. The singlet of methylene protons at C^5 is observed in the spectrum of 4-methoxy derivative **XV** at 2.80 ppm, and in that of 2-methoxy derivative **XVI** at 2.62 ppm in agreement with the criterion suggested for assignment of structures in the series under consideration. In the IR spectra of compounds **XV** and **XVI** are observed absorption bands of carbonyls from acetyl groups at 1700 and 1690 cm^{-1} respectively; in the spectrum of 4-methoxy derivative are present strong bands at 1660 (conjugated carbonyl of the ring) and 1640 cm^{-1} (conjugated double bond), and in the spectrum of 2-methoxy derivative appears a single broad strong band at 1640 cm^{-1} corresponding to the conjugated system including a double bond and a carbonyl group at C^4.

The reaction of enol ethers **XV** and **XVI** with pyrrolidine, *o*-toluidine, and allylamine took several hours at room temperature and furnished compounds **X, XVIIa, b** and **XI**, **XVIIIa, b** in high yield (81–85%). It should be noted here that the physical constants of enaminodiketones **X** and **XI** coincided with those of compounds prepared by acylation of enaminoketones **V** and **IX**. This fact additionally confirms the correctness of the structure assignment to the endocyclic regioisomers. The spectral characteristics of enaminodiketones **XVIIa, b** and **XVIIIa, b** are totally consistent with the assumed structures. In the ^{1}H NMR spectra are retained all the proton signals from the main structural fragments of the molecules, disappear the singlets of methoxy groups, and appear the proton signals from the introduced amino groups, therewith in the spectra of compounds **XIIIb**, **c** and **XIVb, c** which contain an NH group (R = H) is observed a broad singlet of the proton belonging to this group in the region 9–10 ppm. The IR spectra of enaminodiketones **XVa–c** and **XVIa–c** contain the absorption band of enaminoketone moiety at 1675–1620 (conjugated carbonyl of the side chain), 1620–1595 (conjugated carbonyl of the ring), and 1500–1560 cm^{-1} (conjugated double bond), and in the spectra of compounds **XIIIb**, **c** and **XIVb, c** appear also absorption bands of the NH group at 3180–3030 cm^{-1}.

EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from samples pelletized with KBr (for solid substances or from thin films (for fluids). ^{1}H NMR spectra were registered on spectrometer Bruker AT-200 in deuterochloroform solutions using TMS as internal reference. Mass spectra were measured on MKh-1320 instrument. Melting points were measured on Boetius heating block. The reaction progress was monitored and purity of all compounds obtained was checked by TLC on Silufol UV-254 or Alufol UV-254 plates, visualizing of spots under UV light with subsequent spraying with solution of iron(III) chloride. Column chromatography was carried out on silica gel 5/40 μ, 40/100 μ (Chemapol), 40/60 μ (Kieselgel 60, Merck), and neutral aluminum oxide of **II** grade Brockmann activity.

Compounds **IV–VIII** were synthesized as described in [7], and their physical constants were in agreement with those published.

6,6-Dimethyl-2-pyrrolidino-5,6-dihydro-2*H*-thiopyran-4-one (IX). To a solution of 0.94 g of thioether **VIII** in 30 ml of anhydrous benzene was added 0.83 ml (10 mmol) of pyrrolidine. The mixture was boiled under conditions excluding moisture for 8 h and evaporated in a vacuum. The residue was recrystallized from a mixture benzene–hexane to obtain 1.08 g (85%) crystalline enaminoketone **IX**, mp 96–97°C. ^{1}H NMR spectrum, δ, ppm: 1.50 s (6H, Me_2C), 1.98 m (4H, $\underline{CH_2}\underline{CH_2}CH_2$), 2.52 s (2H, CH_2), 3.41 m (4H, CH_2NCH_2), 5.30 s (1H, CH=). IR spectrum, ν, cm^{-1}: 1610, 1550. Found, %: C 62.70; H 8.07; N 6.91; S 15.50. $C_{11}H_{17}NOS$. Calculated, %: C 62.52; H 8.11; N 6.63; S 15.17.

Acylation of regioisomeric pyrrolidine enaminoketones V and IX. To a solution of 0.11 g (0.68 mmol) of the corresponding enaminoketone **V** or **IX** in 20 ml of anhydrous toluene was added 0.16 ml (2.0 mmol) of acetyl chloride and 0.25 g (2.04 mmol) of dimethylaminopyridine. The mixture was boiled under conditions excluding moisture for 10 h and left overnight at room temperature. Then to the reaction mixture was added 30 ml of water, after

stirring the water layer was separated, the organic phase was washed in succession with 10 ml of 2% hydrochloric acid, water, and 2% solution of Na_2CO_3. Then the organic solution was dried on magnesium sulfate, the solvent was evaporated in a vacuum, and the residue was subjected to column chromatography on a column packed with alumina (eluent ethyl acetate–hexane). We obtained 0.95 g (55%) of enaminodiketone **X** or 0.83 g (48%) of enaminodiketone **XI** respectively.

3-Acetyl-6,6-dimethyl-4-pyrrolidino-5,6-dihydro-2*H*-thiopyran-2-one (X). Oily substance. ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, Me_2C), 2.00 m (4H, $\underline{CH}_2\underline{CH}_2CH_2$), 2.46 s (3H, MeCO), 2.92 s (2H, CH_2), 3.40 m (4H, $\underline{CH}_2N\underline{CH}_2$). IR spectrum, ν, cm^{-1}: 1620, 1600, 1515. Found, %: C 61.58; H 7.47; N 5.62; S 12.75. M^+ 253. $C_{13}H_{19}NO_2S$. Calculated, %: C 61.63; H 7.56; N 5.53; S 12.66.

3-Acetyl-6,6-dimethyl-2-pyrrolidino-5,6-dihydro-2*H*-thiopyran-2-one (XI), mp 115–116°C. ^{1}H NMR spectrum, δ, ppm: 1.40 s (6H, Me_2C), 1.96 m (4H, $\underline{CH}_2\underline{CH}_2CH_2$), 2.46 s (3H, MeCO), 2.61 s (2H, CH_2), 3.36 m (4H, $\underline{CH}_2N\underline{CH}_2$). IR spectrum, ν, cm^{-1}: 1650, 1610, 1500. Found, %: C 61.68; H 7.49; N 5.67; S 12.81. M^+ 253. $C_{13}H_{19}NO_2S$. Calculated, %: C 61.63; H 7.56; N 5.53; S 12.66.

3-Acetyl-6,6-dimethyltetrahydrothiopyran-2,4-dione (XIII). To a solution of 1.58 g (10 mmol) of 6,6-dimethyltetrahydrothiopyran-2,4-dione (**VI**) in 40 ml of anhydrous toluene was added at stirring 1 ml (12 mmol) of anhydrous pyridine and 0.80 ml (11 mmol) of acetyl chloride, and the mixture was stirred for 1 h (TLC monitoring). The reaction mixture was washed in succession with 1% solution of HCl, water, Na_2CO_3 solution, and dried with Na_2SO_4. The sodium sulfate was filtered off, and to the obtained toluene solution of O-acyl derivative **XII** was added 2 mmol (0.245 g) of dimethylaminopyridine. The mixture was stirred for 6–8 h with exclusion of moisture (TLC monitoring). The reaction mixture was treated with 10% solution of NaOH till complete extraction of the β-triketone from the organic phase. Then the water solution was acidified with 10% solution of HCl, and triketone was extracted by chloroform (3 × 20 ml). The extract was dried with Na_2SO_4, filtered, and chloroform was removed on a rotary evaporator. The residue was crystallized from ether to obtain 1.32 g (66%) of triketone **XIII**, mp 100–101°C. ^{1}H NMR spectrum, δ, ppm: 1.50 s (6H, Me_2C), 2.58 s (3H, MeCO), 2.96 s (2H, CH_2), 18.40 s (1H, OH enol). IR spectrum, ν, cm^{-1}: 1630, 1560, 1545. Found, %: C 53.79; H 6.11; S 16.20. M^+ 200. $C_9H_{12}O_3S$. Calculated, %: C 53.98; H 6.04; S 16.01.

Exocyclic enaminodiketones XIVa–c. To a solution of 600 mg (3 mmol) of triketone **XIII** in 30 ml of benzene was added an appropriate amine in 1.5 excess, the mixture was boiled for 30 min and left overnight at room temperature. The solvent and excess amine were removed in a vacuum, the residue was diluted with chloroform (30 ml), washed with 10 ml of 2% solution of HCl. The chloroform solution was rapidly dried with magnesium sulfate and passed through a thin bed of silica gel. The solvent was evaporated, and the residue was crystallized from a mixture ethyl acetate–hexane.

6,6-Dimethyl-3-(1-pyrrolidinoethylidene)tetrahydrothiopyran-2,4-dione (XIVa). Yield 0.57 g (75%). mp 134–135°C. ^{1}H NMR spectrum, δ, ppm: 1.46 s (6H, Me_2C), 2.06 m (4H, $\underline{CH}_2\underline{CH}_2CH_2$), 2.50 s (3H, MeCO), 2.70 s (2H, CH_2), 3.60 m and 3.74 m (4H, $\underline{CH}_2N\underline{CH}_2$). IR spectrum, ν, cm^{-1}: 1630, 1580, 1565. Found, %: C 61.76; H 7.41; N 5.70; S 12.43. M^+ 253. $C_{13}H_{19}NO_2S$. Calculated, %: C 61.63; H 7.56; N 5.53; S 12.66.

6,6-Dimethyl-3-(1-*o*-toluidinoethylidene)tetrahydrothiopyran-2,4-dione (XIVb). Yield 0.70 g (80%). mp 138–139°C. ^{1}H NMR spectrum, δ, ppm: 1.50 s (6H, Me_2C), 2.26 s (3H, MeCO), 2.88 s (2H, CH_2), 2.38 s (3H, $\underline{Me}C_6H_4$), 7.30 m (4H, C_6H_4), 8.90 s (^{1}H, NH). IR spectrum, ν, cm^{-1}: 3070, 3030, 1615, 1595, 1565. Found, %: C 66.26; H 6.53; N 4.90; S 11.21. M^+ 289. $C_{16}H_{19}NO_2S$. Calculated, %: C 66.40; H 6.62; N 4.84; S 11.08.

3-(1-Allylaminoethylidene)-6,6-dimethyltetrahydrothiopyran-2,4-dione (XIVc). Yield 0.52 g (72%). mp 74–75°C. ^{1}H NMR spectrum, δ, ppm: 1.46 s (6H, Me_2C), 2.48 s (3H, MeCO), 2.80 s (2H, CH_2), 4.06 t (2H, NCH_2), 5.28 m (2H, $\underline{CH}_2CH=$), 5.90 m (1H, $\underline{CH}=CH_2$), 9.90 s (1H, NH). IR spectrum, ν, cm^{-1}: 3050, 1625, 1580, 1560. Found, %: C 60.12; H 7.21; N 5.79; S 13.53. M^+ 239. $C_{12}H_{17}NO_2S$. Calculated, %: C 60.22; H 7.16; N 5.85; S 13.40.

Enol methyl ethers XV and XVI. (a) In 100 ml of ether was dissolved 1.0 g (5 mmol) of triketone **XIII**, the solution was cooled to 0°C, and at constant stirring was added dropwise an ether solution of diazomethane till complete disappearance of the initial triketone (TLC monitoring). The ether was evaporated, the residue was subjected to column chromatography on silica gel (eluent ethyl acetate–hexane). We obtained 235 mg (22%) of oily 4-methoxy derivative

XV and 355 mg (33%) of crystalline 2-methoxy derivative **XVI**, mp 53–54°C.

3-Acetyl-6,6-dimethyl-4-methoxy-5,6-dihydro-2*H*-thiopyran-2-one (XV). ^{1}H NMR spectrum, δ, ppm: 1.54 s (6H, Me_2C), 2.36 s (3H, MeCO), 2.80 s (2H, CH_2), 3.84 s (3H, OMe). IR spectrum, ν, cm^{-1}: 1700, 1660, 1640. Found, %: C 55.78; H 6.31; S 15.11. M^+ 214. $C_{10}H_{14}O_3S$. Calculated, %: C 56.05; H 6.59; S 14.96.

3-Acetyl-6,6-dimethyl-2-methoxy-5,6-dihydro-2*H*-thiopyran-4-one (XVI). ^{1}H NMR spectrum, δ, ppm: 1.52 s (6H, Me_2C), 2.34 s (3H, MeCO), 2.62 s (2H, CH_2), 3.95 s (3H, OMe). IR spectrum, ν, cm^{-1}: 1690, 1640. Found, %: C 55.95; H 6.44; S 14.81. M^+ 214. $C_{10}H_{14}O_3S$. Calculated, %: C 56.05; H 6.59; S 14.96.

(b) To 50 ml of anhydrous benzene at room temperature while vigorous stirring were added in succession 3.5 g (25 mmol) of freshly calcined K_2CO_3, 0.3 ml (5 mmol) of dimethyl sulfate, and a solution of 1.0 g (5 mmol) of triketone **XIII** in 10 ml of benzene. The stirring was continued for 12 h at room temperature. The solvent was evaporated in a vacuum, the residue was subjected to column chromatography on silica gel (eluent ethyl acetate–hexane). We obtained 500 mg (47%) of methyl ether **XV** and 55 mg (5%) of methyl ether **XVI** identical in all characteristics to compounds obtained along procedure (a).

Reaction of enol methyl ethers XV and XVI with amines. To a solution of 0.10 g (0.47 mmol) of an appropriate methyl ether **XV** or **XVI** in 30 ml of benzene was added a 1.5-fold excess of amine (0.07 mmol, 0.6 ml of pyrrolidine, 0.75 ml of *o*-toluidine, or 0.5 ml of allylamine). The reaction mixture was left standing at room temperature for 8–12 h. The benzene solution was washed with 10 ml of 2% solution of HCl and with water, and dried with sodium sulfate. The benzene was evaporated, and the residue was crystallized from ethyl acetate–benzene mixture to obtain enaminodiketones **X, XVIIa, b, XI, XVIIIa, b.** Compounds **X** and **XI** were obtained in 78 and 80% yield respectively and in all characteristics they were identical to compounds prepared by acylation of enaminoketones **V** and **IX**.

3-Acetyl-6,6-dimethyl-4-(*o*-toluidino)-5,6-dihydro-2*H*-thiopyran-2-one (XVIIa). Yield 115 mg (85%). Oily substance. ^{1}H NMR spectrum, δ, ppm: 1.56 s (6H, Me_2C), 2.16 s (3H, MeCO), 2.84 s (2H, CH_2), 2.30 s (3H, $\underline{Me}C_6H_4$), 7.25 m (4H, C_6H_4), 8.90 s (1H, NH). IR spectrum, ν, cm^{-1}: 1650, 1620, 1540. Found, %: C 66.33; H 6.47; N 4.92; S 11.16. M^+ 289. $C_{16}H_{19}NO_2S$. Calculated, %: C 66.40; H 6.62; N 4.84; S 11.08.

3-Acetyl-6,6-dimethyl-4-allylamino-5,6-dihydro-2*H*-thiopyran-2-one (XVIIb). Yield 90 mg (80%). Oily substance. ^{1}H NMR spectrum, δ, ppm: 1.52 s (6H, Me_2C), 2.50 s (3H, MeCO), 2.80 s (2H, CH_2), 4.01 m (2H, NCH_2), 5.30 m (2H, $\underline{CH}_2CH=$), 5.90 m (1H, $\underline{CH}=CH_2$), 10.10 s (1H, NH). IR spectrum, ν, cm^{-1}: 1655, 1595, 1555. Found, %: C 60.18; H 7.25; N 5.79; S 13.53. M^+ 239. $C_{12}H_{17}NO_2S$. Calculated, %: C 60.22; H 7.16; N 5.85; S 13.40.

3-Acetyl-6,6-dimethyl-2-(o-toluidino)-5,6-dihydro-2*H*-thiopyran-4-one (XVIIIa). Yield 118 mg (87%). mp 120–121°C. ^{1}H NMR spectrum, δ, ppm: 1.42 s (6H, Me_2C), 2.28 s (3H, MeCO), 2.74 s (2H, CH_2), 2.65 s (3H, $\underline{Me}C_6H_4$), 7.25 m (4H, C_6H_4), 8.90 s (1H, NH). IR spectrum, ν, cm^{-1}: 3180, 3080, 1650, 1595, 1560. Found, %: C 66.43; H 6.67; N 4.71; S 11.21. M^+ 289. $C_{16}H_{19}NO_2S$. Calculated, %: C 66.40; H 6.62; N 4.84; S 11.08.

3-Acetyl-6,6-dimethyl-2-allylamino-5,6-dihydro-2*H*-thiopyran-4-one (XVIIIb). Yield 85 mg (76%). mp 54–55°C. ^{1}H NMR spectrum, δ, ppm: 1.48 s (6H, Me_2C), 2.58 s (3H, MeCO), 2.70 s (2H, CH_2), 4.02 m (2H, NCH_2), 5.30 m (2H, $\underline{CH}_2CH=$), 5.90 m (1H, $\underline{CH}=CH_2$), 10.05 s (1H, NH). IR spectrum, ν, cm^{-1}: 1675, 1590, 1560. Found, %: C 60.34; H 7.20; N 5.90; S 13.63. M^+ 239. $C_{12}H_{17}NO_2S$. Calculated, %: C 60.22; H 7.16; N 5.85; S 13.40.

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