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FORMATION OF DERIVATIVES OF 5,6-DIHYDRO-1,3-THIAZINES IN THE REACTION OF ACETOTHIOACETIC ACID ETHYL ESTER UNDER THE CONDITIONS OF THE HANTZSCH SYNTHESIS

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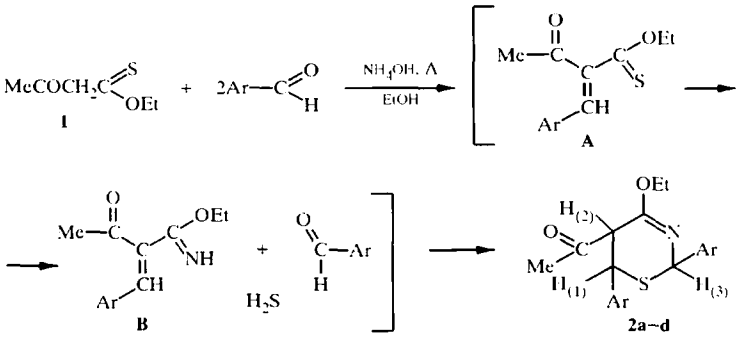
Derivatives of 2H-5,6-dihydro-1,3-thiazine are formed by the reaction of acetothioacetic acid ethyl ester with aromatic aldehydes on heating in ethanol in the presence of aqueous ammonia.

Keywords: 5,6-dihydro-1,3-thiazine, acetothioacetic acid ethyl ester, Hantzsch synthesis

It was shown in [1] that acetothioacetic acid ethyl ester (**1**) on cyclocondensation with aromatic aldehydes and ammonium acetate by heating in acetic acid form symmetrically substituted 1,4-dihydropyridines with ethoxythiocarbonyl substituents in positions 3 and 5. An acid medium is the decisive reaction condition because the interaction of ester **1** with aromatic aldehydes in a molar ratio of 2 : 1 on heating in ethanol in the presence of aqueous ammonia does not lead to a 1,4-dihydropyridine but proceeds in a different way. Acetothioacetic acid ethyl ester **1** containing a reactive thiocarbonyl group reacts with amine and aldehyde components with the elimination of hydrogen sulfide, which in further conversions form 2H-5,6-dihydro-1,3-thiazines (**2**).



a Ar = Ph, **b** 4'-$MeOC_6H_4$, **c** 4'-MeC_6H_4, **d** 4'-BrC_6H_4

The structure of compound **2a** was demonstrated by ^1H and ^{13}C NMR. A completely unambiguous interpretation of the spectra was achieved using selective double resonance for ^{13}C and ^1H. All multiplets in the ^1H NMR spectrum were irradiated selectively and changes were observed in the ^{13}C spectra without decoupling from protons. By this method all the available ^{13}C–H coupling constants were measured through one, two, or three

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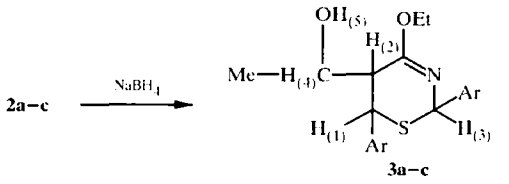
bonds in the molecule. The large value of the coupling constant $J_{H\text{-}1,H\text{-}2}$ = 10.8 Hz corresponds to a *trans* diaxial disposition of these protons, consequently the 5-$COCH_3$ and 6-C_6H_5 substituents are oriented pseudoequatorially. The 2-C_6H_5 group is evidently also equatorially oriented since the homoallyl spin-spin coupling ($J_{H\text{-}2,H\text{-}3}$ = 1.8 Hz) is so large as not to be realized at axial (2-H) and equatorial (3-H) orientations of the interacting protons [2]. The results of the ^{1}H NMR of compounds **2a-d** are in agreement with the structure of thiazine **2** (Table 1). It is impossible to represent the mechanism of forming 1,3-thiazines unequivocally. It may be suggested that the formation of 1,3-thiazines **2** occurs through an arylidene intermediate A and the corresponding imino compound B, which is analogous to the formation of dihydrothiazines by the reaction of ammonia, oxo compounds and β-mercaptoketones [3,4]. Confirmation of the reaction mechanism proposed is the fact that the O-ethyl ester of 2-benzylidenacetothioacetic acid of type A forms thiazine **2a** on reaction with ammonia in ethanol, which is stated in more detail subsequently.

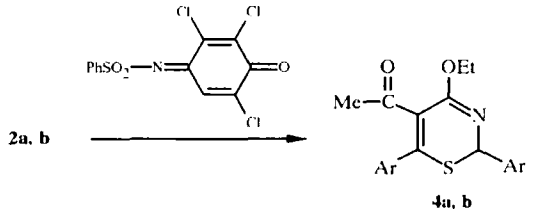
Two characteristic maxima were observed in the IR spectra of compounds **2a-d** at 1640 and 1720 cm^{-1}, which were assigned to the vibration of N=C and C=O bonds. There was no absorption in the 3 μ region. In the electronic absorption spectra there were two absorption maxima in the UV region at 205 nm and a second band with maximum in the range 222-237 nm, which indicates the presence of an aromatic substituent, and also the absence of any conjugated structural fragments. Reduction of **2a-c** with sodium borohydride in a mixture of acetonitrile and methanol in the presence of hydrochloric acid [5] leads to reduction of the carbonyl group in position 5 with the formation of 1,3-thiazin-5-ylcarbinols **3**.



3a–c

a Ar = Ph, **b** 4'-$MeOC_6H_4$, **c** 4'-MeC_6H_4

This reaction also confirms the structure of thiazine **2** because the azomethine bond is readily reduced with sodium borohydride in 4-H-1,3-thiazines [5], but in 2-H-1,3-thiazines the azomethine bond is more stable. Dihydrothiazines **2** are oxidized by substituted 1,4-benzoquinonemonoimines on boiling with the formation of the 1,3-thiazines **4**.



4a, b

a Ar = Ph, **b** 4'-$MeOC_6H_4$

The electronic absorption spectra of compounds **4a,b** have a long wave maximum in the UV region at 402 nm, which indicates the formation of conjugated structural fragments. The IR spectra, ^{1}H and ^{13}C NMR spectra of compounds **4** confirmed their overall structure (see Experimental).

An X-ray structural investigation was carried out to establish the spatial and molecular structure of compound **4a**. The structure of its precursor **2a** was therefore also reliably confirmed. Two independent molecules ***a*** and ***b*** were discovered in the asymmetric portion of the unit cell, linked to a center of pseudosymmetry and differing in the conformations of the heterocyclic rings. The molecules ***a*** and ***b*** in the crystal are shown in Fig. 1. The conformation of the heterocycle in molecule ***a*** is close to a twist form, while in molecule ***b*** it is close to a

TABLE 1. ^{1}H NMR Spectra of 5-Acetyl-2,6-diaryl-4-ethoxy-5,6-dihydro-2H-1,3-thiazines **2**

Compound	Chemical shift, δ, ppm in deuterochloroform, relative to TMS							Coupling constants, J (Hz) $H_{(1)}$–$H_{(2)}$
	CH_2CH_3 (t, 3H)	C(O)–CH_3 (s, 3H)	C–$H_{(1)}$ (d, 1H)	O–CH_2– (q, 2H)	C–$H_{(2)}$ (d, 1H)	C–$H_{(3)}$ (d, 1H)	Ar	
2a*	1.29	2.09	4.0	4.27	4.64	6.11	7.33 (s, 10H)	11.5
2b	1.16	2.0	4.02	4.09	4.58	6.09	3.59 (s, 6H) 6.84; 7.29 (2d, 8H)	11.3
2c	1.27	2.13	3.95	4.22	4.70	6.00	2.31 (s, 6H); 7.22 (s, 8H)	11.4
2d	1.27	2.09	4.0	4.26	4.55	6.10	6.75 (s, 8H)	11.5

* ^{13}C NMR spectrum of compound **2a** ($CDCl_3$), δ, ppm: 205.2 (C=O); 159.9 ($C_{(4)}$); 140.8 ($C_{o'}$); 138.1 (C_o); 128.9; 128.3; 127.4; 126.6 ($C_{o'}$, C_o, $C_{m'}$, C_m); 128.1 ($C_{p'}$); 127.6 (C_p); 63.5 ($C_{(2)}$); 61.5 and 13.9 (OC_2H_5); 57.5 ($C_{(5)}$); 47.3 ($C_{(6)}$); 33.0 (CH_3CO).

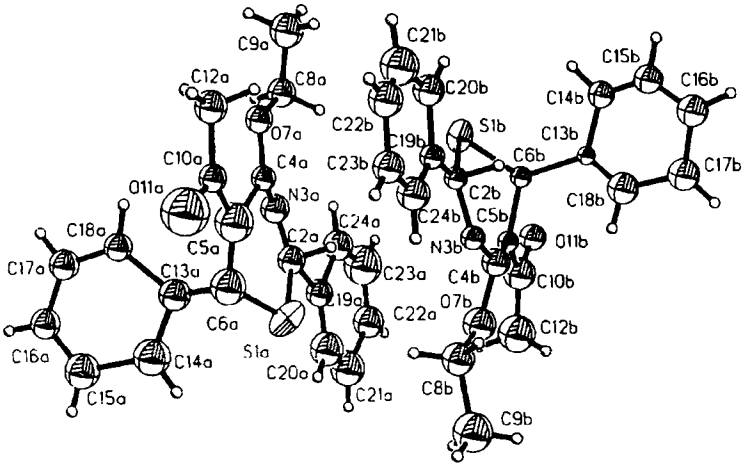
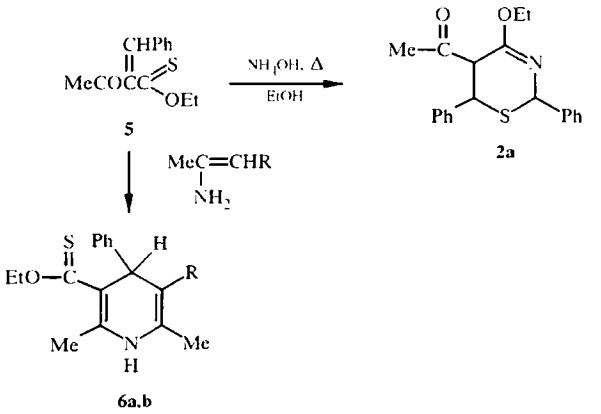


Fig. 1. Molecules ***a*** and ***b*** in the crystal of compound **4a**.

half-chair. The torsion angles of the heterocycle in the molecules ***a*** and ***b*** are given in Table 2. The inclination of the phenyl rings in positions $C_{(12)}$ and $C_{(16)}$ to the mean plane of the heterocycles is characterized by dihedral angles of 13.5(9) and 92.3(9) in molecule ***a*** and 16.5(7) and 96.8(8)° in molecule ***b***.

A mixture of *E*- and *Z*-isomers of 2-benzylidenacetothioacetic acid O-ethyl ester (**5**) is formed in the reaction of acetothioacetic acid O-ethyl ester on cooling in benzene in the presence of piperidine. The separate *E*- and *Z*-forms of compound **5** were obtained by fractional crystallization.



a R = CN; **b** R = COOEt

TABLE 2. Torsion Angles (ω) in the Molecule of **4a**

Angle	ω, deg	
	form *a*	form *b*
$S_{(1)}$–$C_{(2)}$–$N_{(3)}$–$C_{(4)}$	18(3)	4(3)
$C_{(2)}$–$N_{(3)}$–$C_{(4)}$–$C_{(5)}$	-36(3)	3(4)
$N_{(3)}$–$C_{(4)}$–$C_{(5)}$–$C_{(6)}$	9(4)	23(3)
$C_{(4)}$–$C_{(5)}$–$C_{(6)}$–$S_{(1)}$	34(4)	-50(3)
$C_{(5)}$–$C_{(6)}$–$S_{(1)}$–$C_{(2)}$	-42(3)	51(1)
$C_{(6)}$–$S_{(1)}$–$C_{(2)}$–$N_{(3)}$	22(3)	-28(2)

TABLE 3. Coordinates of the Non-hydrogen Atoms ($\times 10^3$) in the Molecule of **4a**

Atom	form *a*			form *b*		
	x	*y*	*z*	*x*	*y*	*z*
1	2	3	4	5	6	7
$S_{(1)}$	-42(1)	471(1)	343(1)	39(1)	873(3)	160(1)
$C_{(2)}$	183(3)	551(2)	278(1)	163(2)	815(1)	227(1)
$N_{(3)}$	-264(3)	648(2)	279(1)	242(2)	701(1)	222(1)
$C_{(4)}$	-223(3)	733(2)	328(1)	237(3)	633(2)	166(1)
$C_{(5)}$	-158(4)	663(3)	394(1)	172(2)	654(1)	110(1)
$C_{(6)}$	-122(4)	534(3)	403(1)	147(2)	799(1)	98(1)
$O_{(7)}$	-293(2)	845(1)	317(1)	252(2)	497(1)	180(1)
$C_{(8)}$	-358(3)	886(2)	256(1)	313(3)	453(2)	245(1)
$C_{(9)}$	-370(4)	1021(3)	261(1)	402(4)	313(3)	246(2)
$C_{(10)}$	-144(3)	768(2)	444(1)	143(3)	558(3)	52(1)
$C_{(11)}$	-92(4)	719(3)	498(1)	86(2)	623(1)	4(1)
$C_{(12)}$	-190(3)	904(2)	443(1)	191(4)	426(3)	61(2)
$C_{(13)}$	-264(3)	480(2)	408(1)	304(2)	884(1)	87(1)
$C_{(14)}$	-267(4)	346(3)	422(1)	291(3)	1019(2)	77(1)
$C_{(15)}$	-449(3)	268(3)	431(1)	397(3)	1077(2)	67(1)
$C_{(16)}$	-584(3)	338(2)	433(1)	539(3)	1037(2)	66(1)
$C_{(17)}$	-581(3)	468(2)	423(1)	570(4)	902(3)	74(1)
$C_{(18)}$	-442(2)	541(2)	415(1)	432(3)	839(3)	88(1)
$C_{(19)}$	-186(3)	460(2)	217(1)	177(2)	872(2)	284(1)
$C_{(20)}$	-132(4)	342(3)	215(2)	135(3)	1004(2)	289(1)
$C_{(21)}$	-152(4)	274(4)	159(2)	148(4)	1058(3)	352(2)
$C_{(22)}$	-218(3)	352(3)	97(2)	201(3)	1005(3)	393(2)
$C_{(23)}$	-268(5)	481(4)	101(2)	253(3)	880(2)	396(1)
$C_{(24)}$	-258(3)	543(3)	161(1)	236(3)	814(3)	337(1)

TABLE 4. Characteristics of the Synthesized 5-Acetyl-2,6-diaryl-4-ethoxy-5,6-dihydro-2H-1,3-thiazines **2a-d**

Compound	Empirical formula	Found, % / Calculated, %				M⁺	mp, °C	Yield, %
		C	H	N	S			
2a	$C_{20}H_{21}NO_2S$	70.5 / 70.8	6.1 / 6.2	3.9 / 4.1	10.1 / 9.5	339	133	56
2b	$C_{22}H_{25}NO_4S$	66.4 / 66.1	6.4 / 6.3	3.4 / 3.5	7.8 / 8.0	367	134	51
2c	$C_{22}H_{25}NO_2S$	72.2 / 71.9	6.9 / 6.8	3.5 / 3.8	8.5 / 8.7	399	141	46
2d	$C_{20}H_{19}Br_2NO_2S$	48.9 / 48.3	4.0 / 3.9	2.7 / 2.8	6.8 / 6.5		143	27

TABLE 5. Characteristics of the Synthesized 2,6-Diaryl-4-ethoxy-5,6-dihydro-2H-1,3-thiazin-5-ylmethylcarbinols **3a-c**

Compound	Empirical formula	Found, % / Calculated, %				mp, °C	Yeild, %
		C	H	N	S		
3a	$C_{20}H_{23}NO_2S$	69.9 / 70.4	6.8 / 6.8	4.6 / 4.1	9.9 / 9.4	97	85
3b	$C_{22}H_{27}NO_4S$	66.0 / 65.8	6.6 / 6.8	3.2 / 3.5	7.6 / 8.0	110	67
3c	$C_{22}H_{27}NO_2S$	71.0 / 71.5	7.4 / 7.4	3.7 / 3.8	8.3 / 8.7	67	84

TABLE 6. ^{1}H NMR Spectra of (2,6-Diaryl-4-ethoxy-5,6-dihydro-2H-1,3-thiazin-5-yl)methylcarbinols **3a-c**

Compound	Chemical shift, δ, ppm (DMSO), relative to TMS									Coupling constants, J (Hz)		
	$OCH_2\underline{CH_3}$ (t, 3H)	$\underline{CH_3}$–$CH_{(4)}$ (d, 3H)	C–$H_{(2)}$ (br. d, 1H)	C–$\underline{H}_{(4)}$ (m, 1H)	–O–CH_2– (q, 2H)	C–$H_{(1)}$ (d, 1H)	$OH_{(5)}$ (d, 1H)	C–$H_{(3)}$ (s, 1H)	Ar	$H_{(1)}$–$H_{(2)}$	$H_{(4)}$–$H_{(3)}$	$H_{(4)}$–CH_3
3a	1.29	1.27	2.8	3.93	4.16	4.67	4.89	5.89	7.31 (s, 10H) 3.53 (s, 3H)	9.0	5.0	6.4
3b	1.27	1.24	2.76	3.91	4.15	4.53	4.86	5.85	7.02 (m, 8H) 2.27 (s, 6H)			
3c	1.27	1.24	2.74	3.91	4.13	4.50	4.86	5.82	7.16 (m, 8H)	9.0	5.0	6.2

Thiazine **2a** was formed on reacting the benzylidene derivative **5** with ammonia in ethanol solution. Reaction with ethyl ester or nitrile of 3-aminocrotonic acid gave 3-ethoxycarbonyl- and 3-cyano-5-ethoxythiocarbonyl-2,6-dimethyl-4-phenyl-1,4-dihydropyridines **6a,b**. The structures of compounds **5** and **6** were confirmed by a combination of physicochemical methods.

EXPERIMENTAL

The IR spectra were obtained on a Perkin–Elmer 580 spectrometer in Nujol, the electronic spectra on a Spectra UV-vis instrument (in ethanol), and the ^{1}H NMR spectra on a Bruker WH-90/DS spectrometer, internal standard was TMS. The mass spectra were taken on an AEI MS 50 instrument. Crystals of compound **4a** of composition $C_{20}H_{19}NO_2S$, grown from a 1 : 1 methanol–chloroform mixture, were monoclinic and had the following crystallographic parameters: a = 8.170(2), b = 10.230(2), c = 21.600(4) Å; β = 100.23(3), V = 1776.6(6) Å^3; M = 337.42; d_{calc} = 1.262 g·cm^{-3}; Z = 4; space group $P2_1$. The intensities of 3039 reflections were measured on a Syntex $P2_1$ automatic diffractometer (MoKα radiation, graphite monochromator, θ/2θ scanning, θ_{max} = 23.5°). The calculations used 1546 independent reflections with $I > 2\sigma(I)$. The structure was solved by the direct method with the SHELXS-86 program [6,7] and was refined by the full matrix least squares method (SHELXL-93) [8] anisotropically for the sulfur atoms and isotropically for the remaining atoms to a final value of 0.092. The coordinates of the non-hydrogen atoms are given in Table 3.

5-Acetyl-2,6-diaryl-4-ethoxy-5,6-dihydro-2H-1,3-thiazines (2a-d). A mixture of acetothioacetic acid O-ethyl ester **1** (2.92 g, 0.02 mol), aromatic aldehyde (0.01 mol), and aqueous ammonia (4 ml) was boiled in ethanol (20 ml) for 30 min. Hydrogen sulfide was evolved. After cooling the mixture was diluted with water. The precipitated oil crystallized from methanol. The characteristics of the compounds synthesized are given in Table 4.

(2,6-Diaryl-4-ethoxy-5,6-dihydro-2H-1,3-thiazin-5-yl)methylcarbinols (3a-c). Sodium borohydride (0.45 g, 0.012 mol) was added in portions to a solution of 5-acetyl-1,3-thiazine (**2a-c**) (0.003 mol) in acetonitrile (10 ml), methanol (2 ml), and conc. hydrochloric acid (1 ml). The mixture was stored at room temperature for 24 h, filtered, the solvent was distilled off in vacuum, and the residue was treated with hot water. Carbinols **3a-c** were separated and crystallized from methanol (Tables 5,6).

5-Acetyl-2,6-diaryl-4-ethoxy-2H-1,3-thiazines (4a,b). 2,3,6-Trichloro-1,4-benzoquinonemono-(N-benzenesulfonyl)imine (1.06 g, 0.003 mol) was added to a solution of 5,6-dihydro-2H-1,3-triazine (**2a,b**) (0.003 mol) in hot benzene (70 ml) and the mixture boiled for 8 h. The solvent was distilled off in vacuum, the residue dissolved in acetone and separated on preparative glass plates of size 220-280 mm in a binder-free layer of silica gel L 40/100 in the system chloroform–hexane–acetone, 9 : 7 : 1. The bright orange band was taken from the plates, extracted with acetone, and the extract evaporated to dryness in vacuum. 2H-1,3-Thiazine **4a** (0.81 g, 80%) was obtained: mp 144°C. UV spectrum, λ_{max}, nm: 205, 276, 325 (sh), 402. IR spectrum, cm^{-1}: 1600, 1620, 1660. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.40 (t, 3H, CH_3); 2.51 (s, 3H, CH_3CO); 4.56 (q, 2H, CH_2); 5.73 (s, 1H, 2-CH); 7.1-8.0 (m, 10H, arom). ^{13}C NMR spectrum ($CDCl_3$ + cyclohexane), δ, ppm: 196.7 (C=O); 163.1 ($C_{(4)}$); 143.3 ($C_{(6)}$); 137.8 ($C_{(i)}$); 133.6 ($C_{(i')}$); 129.5; 129.3; 129.2; 128.2; 127.3 (C_{arom}); 97.6 ($C_{(5)}$); 63.7 (CH_2); 41.5 ($C_{(2)}$); 32.7 ($COCH_3$); 15.7 (CH_3). Mass spectrum, *m/z*: 337 (M^+). Found, %: C 70.9; H 5.8; N 4.5; S 9.2. $C_{20}H_{19}NO_2S$. Calculated, %: C 71.3; H 5.7; N 4.2; S 9.5.

2H-1,3-Thiazine **4b** was obtained analogously in 75% yield; mp 132-134°C (methanol). UV spectrum, λ_{max}, nm: 208, 238, 333 (sh), 402. IR spectrum, cm^{-1}: 1600, 1620, 1650. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.49 (t, 3H, CH_3); 2.62 (s, 3H, CH_3CO); 3.78 (s, 6H, $2OCH_3$); 4.61 (q, 2H, OCH_2); 5.75 (s, 1H, 2-CH); 7.2-7.9 (m, 8H, arom). Found, %: C 66.0; H 6.6; N 3.3; S 7.6. $C_{22}H_{23}NO_4S$. Calculated, %: C 65.8; H 6.8; N 3.5; S 8.0.

2-Benzylidenacetothioacetic Acid (*Z,E*)-O-Ethyl Ester (5). Benzaldehyde (2.12 g, 0.02 mol) and piperidine (3 drops) were added to a solution of freshly distilled acetothioacetic acid O-ethyl ester (2.92 g, 0.02 mol) in dry benzene (10 ml). The reaction mixture was maintained at 0°C for 48 h, dried with anhydrous sodium sulfate, and the solvent removed in vacuum. The orange oil was distilled and the fraction collected with bp 155-160°C/10 mm Hg. An orange oil (3.46 g, 74%) was obtained which consisted of the *Z*- and *E*-forms of **5** in a ratio 1 : 1 (HPLC). The *Z*-form (1.6 g, 34%) of mp 62-68°C was obtained by fractional crystallization from ethanol

at -5 to -10°C as bright yellow crystals. UV spectrum, λ_{max}, nm: 202, 232, 253, 297. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 (t, 3H, CH_2CH_3); 2.42 (s, 3H, CH_3CO); 4.69 (q, 2H, OCH_2); 7.36 (s, 5H, arom); 7.42 (s, 1H, CH=). Mass spectrum, *m/z*: 234 (M^+). Found, %: C 66.8; H 6.2; S 13.2. $C_{13}H_{14}O_2S$. Calculated, %: C 66.6; H 6.0; S 13.7. After extended cooling of the ethanolic filtrate dark yellow crystals (*E*-form) separated, yield 1.2 g (26%); mp 58-60°C. Found, %: C 66.5; H 6.1; S 13.2. $C_{13}H_{14}O_2S$. Calculated, %: C 66.6; H 6.0; S 13.7. UV spectrum, λ_{max}, nm: 202, 236, 326. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.44 (t, 3H, CH_2CH_3); 2.33 (s, 3H, CH_3CO); 4.60 (q, 2H, OCH_2); 7.33 (s, 5H, arom), 7.69 (s, 1H, CH=). Mass spectrum, *m/z*: 234 (M^+).

5-Acetyl-4-ethoxy-2,6-diphenyl-5,6-dihydro-2H-1,3-thiazine (2a). Ammonium hydroxide (25%, 0.34 ml) was added to a solution of 2-benzylidenacetothioacetic acid (*Z,E*)-O-ethyl ester **5** (0.23 g, 0.001 mol) in ethanol (3 ml) and the mixture boiled for 5 min. Clarification of the solution occurred and hydrogen sulfide was evolved (confirmed with lead acetate paper). White crystals separated after cooling. Thiazine **2a** (0.13 g, 76%) was obtained, the properties and physicochemical characteristics of which corresponded with those described previously.

3-Cyano-5-ethoxythiocarbonyl-2,6-dimethyl-4-phenyl-1,4-dihydropyridine (6a). A mixture of benzylidenacetothioacetic acid O-ethyl ester **5** (2.34 g, 0.01 mol) and 3-aminocrotonic acid nitrile (1.0 g, 0.012 mol) in 2-propanol (50 ml) with added acetic acid (5 ml) was boiled for 10 h. The solvents were removed in vacuum, and the residue crystallized from methanol. 1,4-Dihydropyridine **6a** (1.4 g, 47%) was obtained; mp 218-220°C. UV spectrum, λ_{max}, nm: 207, 280, 405. IR spectrum, ν, cm^{-1}: 1625, 1650, 2230, 3320. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.24 (t, 3H, CH_3); 2.18 (s, 3H, 2-CH_3); 2.30 (s, 3H, 6-CH_3); 3.99 (q, 2H, OCH_2); 5.44 (s, 1H, 4-CH); 7.15 (s, 5H, arom); 9.25 (s, 1H, N-H). Found, %: C 68.1; H 6.2; N 9.1; S 10.9. $C_{17}H_{18}N_2OS$. Calculated, %: C 68.4; H 6.1; N 9.4; S 10.8.

3-Ethoxycarbonyl-5-ethoxythiocarbonyl-2,6-dimethyl-4-phenyl-1,4-dihydropyridine (6b). A mixture of 2-benzylidenacetothioacetic acid O-ethyl ester **5** (2.34 g, 0.01 mol) and β-aminocrotonic acid ethyl ester (1.3 g, 0.01 mol) in ethanol (50 ml) and acetic acid (5 ml) was boiled for 5 h. The solvents were removed in vacuum, and the residue treated with ether. Yellow crystals were obtained. Yield 2.1 g (60.8%); mp 120°C (ethanol). UV spectrum, λ_{max}, nm: 207, 280, 405. IR spectrum, ν, cm^{-1}: 1615, 1640, 1690, 3400. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.13 (t, 3H, CH_3); 1.27 (s, 3H, $C(S)OCH_2\underline{C}H_3$); 2.20 (s, 3H, 2-$CH_3$); 2.31 (s, 3H, 6-$CH_3$); 3.96 (q, 2H, $-CH_2$); 4.36 (q, 2H, $C(S)OCH_2$); 5.47 (s, 1H, 4-CH); 7.11 (s, 5H, arom); 9.04 (s, 1H, N-H). Mass spectrum, *m/z*: 345 (M^+). Found, %: C 66.3; H 6.7; N 3.9; S 9.4. $C_{19}H_{23}NO_3S$. Calculated, %: C 66.1; H 6.7; N 4.1; S 9.3.

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