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SYNTHESIS OF SOME NEW 4,5-DISUPSTITUTED-2,4-DIHYDRO--3H-1,2,4-TRIAZOLINE-3-THIONES

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A number of 4,5-disupstituted 2,4-dihydro-3H-1,2,4-triazoline-3-thiones (Scheme 1) were obtained by the oxidative cyclization of the appropriate 2-, 3-, 4-hydroxybenzoyl-, 2-hydroxy-5-chlorobenzoyl-, 3,4,5-trimethoxybenzoyl- and 4-hydroxy- and 4-ethoxyphenacethyl-4-*n*-butyl/phenylthiosemicarbazides. Their structure was determined by UV, IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

Key words: supstituted benzoyl/phenacetyl hydrazines; supstituted benzoyl/phenacetyl-4-alkyl/phenyl thiosemicarbazides; 1,2,4-triazoline-3-thions

INTRODUCTION

1,2,4-Triazole and its derivatives represent one of the most active class of compounds possessing a wide spectrum of biological activity (antibacterial, antifungal, hypoglycaemic, antihypertensive) [1–5].

On the other hand, it is reported in the literature that the antiviral [6] and antibacterial [7, 8] activities of thiourea derivatives was due to the -NH-C(S)-NH- function in the molecule and that the changes in this activity depended on its supstituents. The above observation and in continuation of our work on the synthesis of heterocycles [9, 10, 11], we report here the synthesis of some new triazoline-3-thiones with the same pharmaphoric group and with the view of studying their antimicrobial and antifungal activities against some microorganisms.

EXPERIMENTAL

The melting points of synthesized compounds were determined on a Büchi 510 melting point apparatus and therefore the values reported here are uncorrected. The IR spectra were recorded in the range of 4000-400 cm^{-1} using the KBr disks on a Perkin-Elmer 297 Spectrophotometer. The ^{1}H (250 MH$_z$) NMR spectra were recorded with a Bruker AC 250E spectrometer in DMSO-d$_6$ with TMS as an internal standard. UV spectra were recorded on a Varian Cary 219 spectrophotometer.

Supstituted benzoyl/phenacetyl hydrazines (2)

They were synthesized by hydrazinolysis of the methyl/ethyl esters following the literature methods [12, 13, 14].

General procedure of 1-(supstituted benzoyl/phenacetyl-4-n-butyl/phenyl thiosemicarbazides (3)

A mixture of 2 (0.01 mol) and *n*-butyl/phenyl-isothiocyanate (0.01 mol) in 120 ml ethanol was heated under reflux for 2–3 hours. The excess of ethanol was removed by distilling under reduced pressure. The white precipitate was washed with ethanol and recrystalized from ethanol.

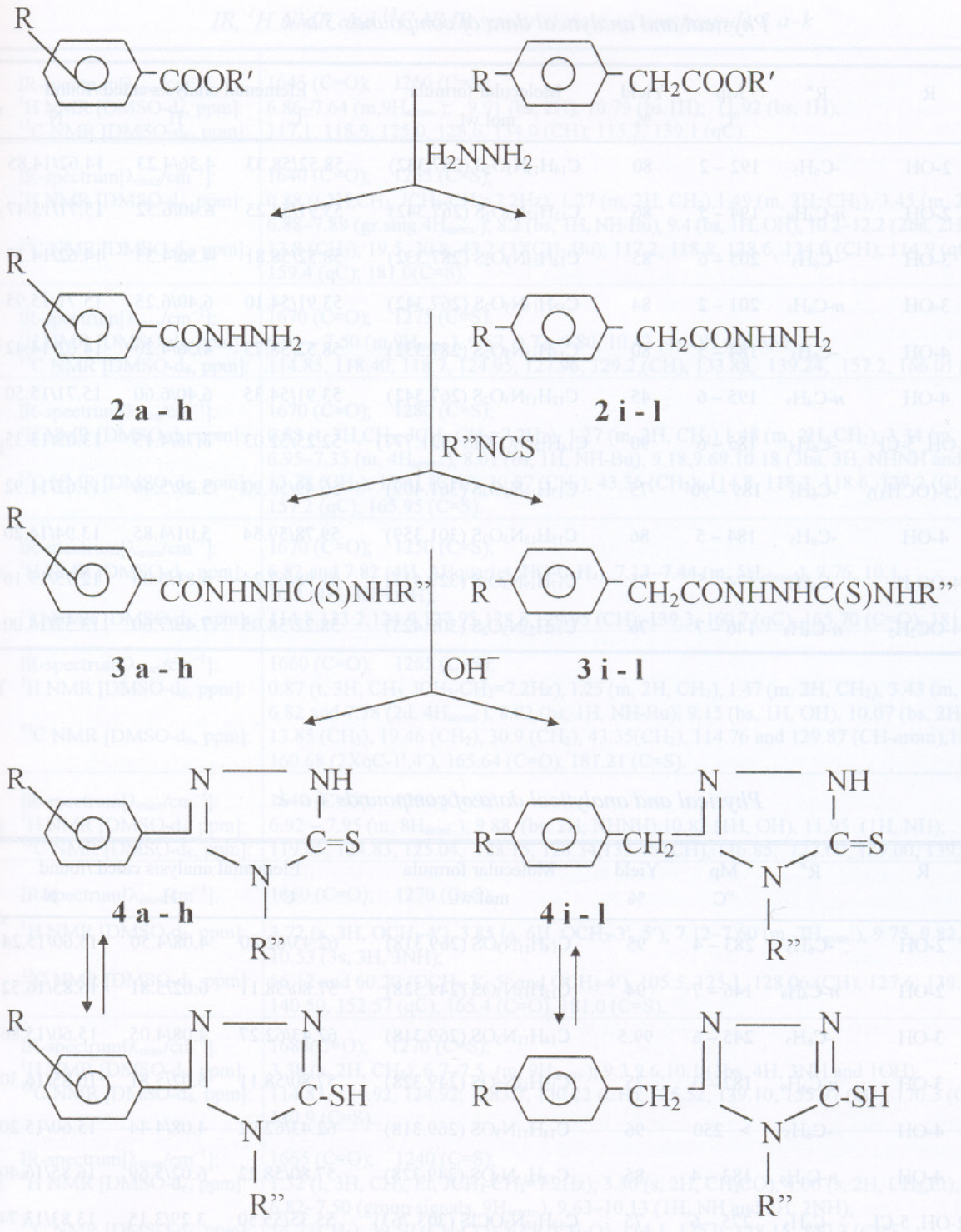
General procedure of 4,5-disupstituted-2,4-dihydro-3H-1,2,4-triazoline-3-thiones (4)

A mixture of 3 (0.005 mol) and NaOH solution (2M, 15 ml) was refluxed for 4 hours. On cooling, it was solidified (sodium salt of 4). This was dissolved in cold ice water and acidified with hydrochloric acid to pH 5–6. The solid which appeared was filtered, washed with water (neutral pH), dried and recrystalized from appropriate solvent.

RESULTS AND DISCUSSION

Oxidative cyclization of (3 a–k) with 2M NaOH solution gave 4,5-disupstituted-2,4-dihydro-3H-1,2,4-triazoline-3-thiones (4 a–k) in a pure state according to the route presented in Scheme 1.

In order to achieve this purpose, it was necessary to synthesize a number hydrazides (2) of some hydroxy- and methoxy or ethoxy supstituted benzoic and phenylacetic acids. The compounds (2) were readily prepared by hydrazinolysis of the corresponding methyl/ethyl esters. Next derivatives (2) were converted into the 1-(supstituted benzoyl/phenacetyl-4-*n*-butyl/phenylthiosemicarbazides (3) by refluxing with *n*-butyl- or phenylisothiocyanates in ethanolic solution. The melting points, yield and elemental analysis of (3) are given in Table 1. The structure of (3) was established by IR, ^{1}H NMR and ^{13}C NMR spectra (Table 3). The IR absorptions due to NH/NH, C=O and C=S functions appeared at 3350/3150, 1680/1640 and 1290/1250 cm^{-1}, respectively. The absorption bands associated with other functional groups appeared in the expected regions. The ^{1}H NMR spectra of compounds (3) exhibited a multiplet in the aromatic region accounting for $H_{arom.}$ protons at 6.80–7.90 ppm. Three or four low fields singlets were observed in the 8.01–12.2 ppm region accounting for protons of OH group and NH (thiosemicarbazide moiety). The H of NHNH sandwiched between thiocarbonyl and supstituted benzoyl/phenacetyl group have resonated at a low fields position (~ 12 ppm) due to the strong deshielding effect of the aromatic ring system and thiocarbonyl group. When compounds (3) were refluxed in 2M NaOH solution for about 4 hours, 4,5-disupstituted-2,4-dihydro-3H-1,2,4-triazoline-3-thiones were produced (4) in good yields. The reaction of oxidative cyclization of thiosemicarbazides have been described earlier [15–17]. We were interested to see if cyclization of this type could be extended to constitute a general approach for the synthesis of other 1,2,4-triazoline-3-thions derivatives utilizing hydroxy- and methoxy/ethoxybenzoyl/phenacetyl hydrazines as starting materials. All the synthesized new compounds (4) were obtained in the form of high melting solids. Satisfactory spectroscopic and analytical data were obtained for all compounds 4, (Tables 2 and 4). The spectral data were in good agreement with, and hence support, the proposed structure. While it is possible to consider that the 1,2,4-triazoline-3-thions may exist in **thion-thiol** tautomeric forms our chemical and spectral investigations showed that the thion structure dominates. The UV spectra of (4) showed two absorption maxima or shoulders at 250–267 and 282–290 nm. These data indicated that some of these compounds exist predominantly in thion form in ethanolic solution [18, 19]. The absorption at 282–290 nm indicated the presence of a chromophoric C=S group. In addition to the UV date, the IR and NMR data of compounds (4) support the thion form in the solid state and in nonpolar solvent; their IR spectra in KBr disk showed multiple combination of NH bands in the 3380–3300 cm^{-1} region and showed no absorption bands about 2600–2550 cm^{-1} which is indicative of the thiol form; the IR absorption due to C=S functions in (4) appeared at about 1300 cm^{-1} [8, 20]. The ^{1}H NMR spectra of (4) in DMSO-d_6 exhibited the NH signals (NH function of the triazoline ring) as singlet or a broad peaks between 13.55 and 14.10 ppm supported the thion structure [21, 22]. The signals associated with other functional groups appeared in the expected regions.



$R' = -CH_3, -CH_2CH_3$; $R'' = n\text{-}C_4H_9, -C_6H_5$

Scheme 1

Table 1

Physical and analytical data of compounds 3 a–k

Compound	R	R″	Mp °C	Yield %	Molecular formula mol.wt.	Elemental analysis calcd./found C	H	N
3a	2-OH	-C_6H_5	192 – 2	80	$C_{14}H_{13}N_3O_2S$ (287.332)	58.52/58.33	4.56/4.23	14.62/14.85
3b	2-OH	*n*-C_4H_9	194 – 5	86	$C_{12}H_{17}N_3O_2S$ (267.342)	53.91/54.25	6.40/6.32	15.71/15.47
3c	3-OH	-C_6H_5	205 – 6	85	$C_{14}H_{13}N_3O_2S$ (287.332)	58.52/58.81	4.56/4.33	14.62/14.37
3d	3-OH	*n*-C_4H_9	201 – 2	84	$C_{12}H_{17}N_3O_2S$ (267.342)	53.91/54.10	6.40/6.25	15.71/15.95
3e	4-OH	-C_6H_5	184 – 5	80	$C_{14}H_{13}N_3O_2S$ (287.332)	58.52/58.75	4.56/4.20	14.62/14.42
3f	4-OH	*n*-C_4H_9	195 – 6	45	$C_{12}H_{17}N_3O_2S$ (267.342)	53.91/54.35	6.40/6.60	15.71/15.50
3g	2-OH, 5-Cl	-C_6H_5	185 – 6	90	$C_{14}H_{12}N_3O_2ClS$ (321.777)	52.25/52.03	3.75/4.15	13.05/13.35
3h	3,4,5-$(OCH_3)_3$	-C_6H_5	189 – 90	75	$C_{17}H_{19}N_3O_4S$ (361.409)	56.49/56.90	5.29/5.46	11.62/11.92
3i	4-OH	-C_6H_5	184 – 5	86	$C_{15}H_{15}N_3O_2S$ (301.359)	59.78/59.54	5.01/4.85	13.94/14.20
3j	4-OC_2H_5	-C_6H_5	174 – 5	75	$C_{17}H_{19}N_3O_2S$ (329.413)	61.98/62.24	5.81/6.06	12.75/13.16
3k	4-OC_2H_5	*n*-C_4H_9	146 – 7	76	$C_{15}H_{23}N_3O_2S$ (309.423)	58.22/58.05	7.49/7.60	13.57/14.00

Table 2

Physical and analytical data of compounds 4 a–k

Compound	R	R″	Mp °C	Yield %	Molecular formula mol.wt.	Elemental analysis calcd./found C	H	N
4a	2-OH	-C_6H_5	283 – 4	95	$C_{14}H_{11}N_3OS$ (269.318)	62.43/62.80	4.08/4.50	15.60/15.24
4b	2-OH	*n*-C_4H_9	146 – 7	94	$C_{12}H_{15}N_3OS$ (249.328)	57.80/58.11	6.02/5.81	16.85/16.52
4c	3-OH	-C_6H_5	245 – 6	99.5	$C_{14}H_{11}N_3OS$ (269.318)	62.43/62.27	4.08/4.05	15.60/15.86
4d	3-OH	*n*-C_4H_9	182 – 3	75	$C_{12}H_{15}N_3OS$ (249.328)	57.80/58.11	6.02/5.81	16.85/16.30
4e	4-OH	-C_6H_5	> 250	96	$C_{14}H_{11}N_3OS$ (269.318)	62.43/62.92	4.08/4.44	15.60/15.20
4f	4-OH	*n*-C_4H_9	183 – 4	85	$C_{12}H_{15}N_3OS$ (249.328)	57.80/58.22	6.02/5.69	16.85/16.40
4g	2-OH, 5-Cl	-C_6H_5	275 – 6	75	$C_{14}H_{10}N_3OClS$ (303.763)	55.35/55.50	3.29/3.15	13.83/13.74
4h	3,4,5-$(OCH_3)_3$	-C_6H_5	208 – 9	91	$C_{17}H_{17}N_3O_3S$ (343.395)	59.46/59.05	4.99/5.40	12.23/11.84
4i	4-OH	-C_6H_5	210 – 11	88	$C_{15}H_{13}N_3OS$ (285.345)	63.53/63.80	4.58/5.08	14.82/14.65
4j	4-OC_2H_5	-C_6H_5	194 – 5	90	$C_{17}H_{17}N_3OS$ (311.399)	65.57/65.86	5.50/5.43	13.49/14.00
4k	4-OC_2H_5	*n*-C_4H_9	105 – 6	87	$C_{15}H_{21}N_3OS$ (291.409)	61.82/62.05	7.26/6.88	14.41/14.85

Table 3

IR, ^1H NMR and ^{13}C NMR spectral data of compounds 3 a–k

3a	IR-spectrum[λ_{max}/cm^{-1}]:	1645 (C=O); 1260 (C=S);
	^1H NMR [DMSO-d_6, ppm]:	6.86–7.64 (m,9$H_{arom.}$); 9.91 (bs, 2H); 10.79 (bs.1H); 11.92 (bs, 1H);
	^{13}C NMR [DMSO-d_6, ppm]:	117.1, 118.9, 125.0, 128.6, 134.0 (CH); 115.2, 139.1 (qC).
3b	IR-spectrum[λ_{max}/cm^{-1}]:	1640 (C=O); 1265 (C=S);
	^1H NMR [DMSO-d_6, ppm]:	0.88 (t,3H,CH_3, JCH_3-CH_2=7.2Hz), 1.27 (m, 2H, CH_2),1,49 (m, 2H, CH_2), 3.45 (m, 2H, CH_2), 6.88–7.89 (gr.sing.4$H_{arom.}$); 8.2 (bs, 1H, NH-Bu), 9.4 (bs, 1H, OH), 10.2–12.2 (2bs, 2H, NHNH);
	^{13}C NMR [DMSO-d_6, ppm]:	13.8 (CH_3); 19.5, 30.8, 43.2 (3XCH_2,Bu); 117.2, 118.8, 128.6, 134.0 (CH); 114.9 (qC), 159.4 (qC); 181.0(C=S).
3c	IR-spectrum[λ_{max}/cm^{-1}]:	1670 (C=O); 1275 (C=S);
	^1H NMR [DMSO-d_6, ppm]:	6.91 – 7.50 (m,9$H_{arom.}$), 9.67, 9.72, 9.80, 10.42 (4s,OH and 3NH);
	^{13}C NMR [DMSO-d_6, ppm]:	114.85, 118.40, 118.7, 124.95, 127.96, 129.2,(CH), 133.88, 139.24, 157.2, 166.01 (qC).
3d	IR-spectrum[λ_{max}/cm^{-1}]:	1670 (C=O); 1280 (C=S);
	^1H NMR [DMSO-d_6, ppm]:	0.88 (t, 3H,CH_3, JCH_3-CH_2=7.2Hz), 1.27 (m, 2H, CH_2),1,48 (m, 2H, CH_2), 3.34 (m, 2H, CH_2), 6.95–7.35 (m, 4$H_{arom.}$), 8.01 (bs, 1H, NH-Bu), 9.18,9.69.10.18 (3bs, 3H, NHNH and OH);
	^{13}C NMR [DMSO-d_6, ppm]:	13.78 (CH_3); 19.41 (CH_2); 30.87 (CH_2); 43.35 (CH_2); 114.8, 118.3, 118.6, 129.2 (CH); 133.1, 157.2 (qC); 165.95 (C=S).
3e	IR-spectrum[λ_{max}/cm^{-1}]:	1670 (C=O); 1250 (C=S);
	^1H NMR [DMSO-d_6, ppm]:	6.82 and 7.82 (4H, ABquartet, HO-C_6H_4), 7.13–7.44 (m, 5H_{phenyl}), 9.76, 10.1, 10.3 (4H, 3NH,OH);
	^{13}C NMR [DMSO-d_6, ppm]:	114.8,123.2,124.9,127.95,128.8,129.95 (CH); 139.3, 160.7 (qC), 165.70 (C=O); 181.22 (C=S).
3f	IR-spectrum[λ_{max}/cm^{-1}]:	1660 (C=O); 1265 (C=S);
	^1H NMR [DMSO-d_6, ppm]:	0.87 (t, 3H, CH_3, JCH_3-CH_2=7.2Hz), 1.25 (m, 2H, CH_2), 1.47 (m, 2H, CH_2), 3.43 (m, 2H, CH_2), 6.82 and 7.78 (2d, 4$H_{arom.}$), 8.02 (bs, 1H, NH-Bu), 9.15 (bs, 1H, OH), 10.07 (bs, 2H, NHNH);
	^{13}C NMR [DMSO-d_6, ppm]:	13.85 (CH_3), 19.46 (CH_2), 30.9 (CH_2), 43.35(CH_2), 114.76 and 129.87 (CH-arom),123.14, 160.68 (2XqC-1′,4′), 165.64 (C=O), 181.21 (C=S).
3g	IR-spectrum[λ_{max}/cm^{-1}]:	1640 (C=O); 1290 (C=S);
	^1H NMR [DMSO-d_6, ppm]:	6.92 – 7.95 (m, 8$H_{arom.}$), 9.88, (bs. 2H, NHNH),10.82 (1H, OH), 11.95 (1H, NH);
	^{13}C NMR [DMSO-d_6, ppm]:	119.05, 124.83, 125.04, 128.15, 128.34,133.46 (CH), 116.85, 122.60, 139.00, 139.12 (qC).
3h	IR-spectrum[λ_{max}/cm^{-1}]:	1660 (C=O); 1270 (C=S);
	^1H NMR [DMSO-d_6, ppm]:.	3.72 (s, 3H, OCH_3-4′), 3.85 (s, 6H, OCH_3-3′, 5′), 7.12–7.60 (m, 7$H_{arom.}$), 9.75, 9.82, 10.53 (3s, 3H, 3NH);
	^{13}C NMR [DMSO-d_6, ppm]:	56.12 and 60.20 (OCH_3-3′, 5′ and OCH_3-4′), 105.5, 125.1, 128.06 (CH), 127.6, 139.27, 140.50, 152.57 (qC), 165.4 (C=O), 181.0 (C=S).
3i	IR-spectrum[λ_{max}/cm^{-1}]:	1680(C=O); 1270 (C=S);
	^1H NMR [DMSO-d_6, ppm]:	3.38 (s, 2H, CH_2); 6.7–7.5 (m, 9$H_{arom.}$); 9.3,9.6,10.1 (3bs, 4H, 3NH and 1OH);
	^{13}C NMR [DMSO-d_6, ppm]:	114.83, 114.92, 124.92, 128.07, 130.22 (CH); 125.52, 139.10, 155.97 (qC); 170.3 (C=O), 180.9 (C=S).
3j	IR-spectrum[λ_{max}/cm^{-1}]:	1665 (C=O); 1240 (C=S);
	^1H NMR [DMSO-d_6, ppm]:	1.32 (t, 3H, CH_3, Et, JCH_3-CH_2=7.2Hz); 3.30 (s, 2H, CH_2CO); 4.00 (s, 2H, CH_2,Et), 6.82–7.50 (group signals, 9$H_{arom.}$), 9,63–10.13 (1H, NH and 2H, 2NH);
	^{13}C NMR [DMSO-d_6, ppm]:	14.7 (CH_3); 39.50 (CH_2CO), 62.9 (CH_2O), 114.1, 125.0, 128.15, 130.3 (CH), 127.3, 139.1, 157.3 (qC), 170.3 (C=O), 181.0(C=S).
3k	IR-spectrum[λ_{max}/cm^{-1}]:	1670 (C=O); 1240 (C=S);
	^1H NMR [DMSO-d_6, ppm]:	0.87 (t, 3H, CH_3), 1.25 (m, 2H, CH_2), 1.30 (t, 3H, CH_3, OEt), 1.44 (m, 2H, CH_2), 3.33 (s, 2H, CH_2, CH_2CO), 3.43 (t, 2H, CH_2), 3.98(q, 2H, CH_2, OEt), 6.84 and 7.18 (ABpatern, 4$H_{arom.}$), 7.78(bs, 1H, NH) 9.11 and 9.85 (2bs, 2H, NHNH);
	^{13}C NMR [DMSO-d_6, ppm]:	13.8 (CH_3Bu), 14.7 (CH_3,EtO), 19.45(CH_2), 30.90(CH_2), 39.9(CH_2, CH_2CO), 43.4(CH_2, NCH_2), 62.95(CH_2O), 114.13, 130.27 (CH), 127.3, (qC-1′), 157.28 (qC-4′), 170.2(C=O), 181.5(C=S).

Table 4

IR, UV, ^{1}H NMR and ^{13}C NMR spectral data of compounds 4 a–k

4a	IR-spectrum[λ_{max}/cm^{-1}]:	1480(C=N); 1320 (C=S);
	UV[EtOH, λ/nm]:	255; 266; 285;
	^{1}H NMR [DMSO-d$_6$, ppm]:.	6.70–7.40(m, 9H$_{arom.}$), 9.91 (s, 1H, OH), 14.0(bs, 1H, NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	115.6, 118.8, 127.8, 128.5, 128.7, 132.0(CH), 113.3, 134.3, 149.7, 155.8(qC), 167.6(C=S).
4b	IR-spectrum[λ_{max}/cm^{-1}]:	1490 (C=N); 1300 (C=S);
	UV[EtOH, λ/nm]:	255; 285;
	^{1}H NMR [DMSO-d$_6$, ppm]:	0.67 (t, 3H, CH$_3$, JCH$_3$-CH$_2$=7.2Hz), 1.05 (m, 2H, CH$_2$), 1.45 (m, 2H, CH$_2$), 3.86 (t, 2H, CH$_2$), 6.89–7.47 (m, 4H$_{arom.}$), 10.37 (bs. 1H, OH), 13.83 (bs, 1H, NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	13.2 (CH$_3$), 19.0 (CH$_2$-3), 29.5 (CH$_2$-2), 43.3 (CH$_2$-1), 116.0, 119.4, 131.5, 132.5 (CH), 113.5, 150.0, 155.8 (qC), 166.47(C=S).
4c	IR-spectrum[λ_{max}/cm^{-1}]:	1500 (C=N); 1340 (C=S);
	UV[EtOH, λ/nm]:	250; 263; 282;
	^{1}H NMR [DMSO-d$_6$, ppm]:	6.60–7.58 (m, 9 H$_{arom.}$), 9.73 (bs, 1H, OH) 14.1(bs, 1H, NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	115.1, 117.3, 118.8, 128.6, 129.3,129.4,129.6(CH), 126.83, 134.6, 150.5, 157.2 (qC), 168.6 (C=S).
4d	IR-spectrum[λ_{max}/cm^{-1}]:	1480 (C=N); 1300 (C=S);
	UV[EtOH, λ/nm]:	256; 286;
	^{1}H NMR [DMSO-d$_6$, ppm]:	0.75 (t, 3H, CH$_3$, JCH$_3$-CH$_2$=7.2Hz), 1.13 (m, 2H, CH$_2$-3), 1, 49 (m, 2H, CH$_2$-2), 4.01 (t, 2H, CH$_2$-1), 7.00–7.35 (m, 4H$_{arom.}$), 9.89 (bs, 1H, NH), 13.84 (bs, 1H, NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	13.2 (CH$_3$); 18.98, 29.52, 43.38 (3XCH$_2$,Bu); 115.2, 117.7, 119.0, 130.2 (CH); 127.24, 151.2, 157.6, 167.0 (qC).
4e	IR-spectrum[λ_{max}/cm^{-1}]:	1500 (C=N); 1330 (C=S);
	UV[EtOH, λ/nm]:	255; 267; 285;
	^{1}H NMR [DMSO-d$_6$, ppm]:	6.68 and 7.09(4H , ABq), 7.17 – 7.56 (5H$_{arom.}$), 10.0 (bs,1H, OH),14.00(bs, 1H, NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	115.3,128.8,129.3,129.8, (CH); 116.3, 134.8,150.7,159.2,168.2 (qC).
4f	IR-spectrum[λ_{max}/cm^{-1}]:	1515 (C=N); 1300 (C=S);
	UV[EtOH, λ/nm]:	256;
	^{1}H NMR [DMSO-d$_6$, ppm]:	0.75 (t, 3H, CH$_3$, JCH$_3$-CH$_2$=7.2Hz), 1.12 (m, 2H, CH$_2$), 1,50 (m, 2H, CH$_2$), 4.00 (t, 2H. CH$_2$), 6.91, 7.47 (2d, 4H$_{arom.}$), 10.20 (bs, 1H, OH), 13.80 (bs, 1H, NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	13.3 (CH$_3$), 19.0, 29.5, 43.3 (3XCH$_2$, Bu), 115.8, 130.2 (CH), 116.7, 151.4, 159.5 (qC), 166.76 (C=S).
4g	IR-spectrum[λ_{max}/cm^{-1}]:	1490 (C=N); 1330 (C=S);
	UV[EtOH, λ/nm]:	254; 290;
	^{1}H NMR [DMSO-d$_6$, ppm]:	6.72 – 7.42 (m, 8H$_{arom.}$), 10.26, (bs, 1H, OH),14.10 (bs, 1H,NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	117.3, 127.8, 128.6, 128.80, 130.8, 131.9 (CH), 114.9, 122.1, 134.2, 148.4, 154.9 (qC),167.7(C=S).
4h	IR-spectrum[λ_{max}/cm^{-1}]:	1510 (C=N); 1330 (C=S);
	UV[EtOH, λ/nm]:	260; 290;
	^{1}H NMR [DMSO-d$_6$, ppm]:	3.75 (s, 6H, 2MeO-3',5'), 3.86 (s,3H, EtO-4'), 6.60(s,2H$_{arom.}$-2',6'), 7.31–7.62 (m, 5H$_{arom.}$) 14.10(bs, 1H,NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	55.6 (2X MeO), 60.06 (1X MeO); 150.6,128.9,129.1(CH); 120.7, 134.9, 138.9,150.1(qC), 152.6, (2XqC), 168.6 (C=S).
4i	IR-spectrum[λ_{max}/cm^{-1}]:	1500 (C=N); 1300 (C=S);
	UV[EtOH, λ/nm]:	225; 253;
	^{1}H NMR [DMSO-d$_6$, ppm]:	3.73 (s, 2H, ArCH$_2$), 6.63 (4H, ABq), 7.20–7.47 (5H$_{phenyl}$), 9.31 (s, 1H, OH), 13.79 (s, 1H, NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	30.6(CH$_2$), 115.1, 128.2, 129.2, 129.3, 129.5(CH), 124.4, 133.6, 151.7, 156.1, 167.8 (qC).
4j	IR-spectrum[λ_{max}/cm^{-1}]:	1510 (C=N); 1300 (C=S);
	UV[EtOH, λ/nm]:	232; 261;
	^{1}H NMR [DMSO-d$_6$, ppm]:.	1.27 (t, 3H, CH$_3$,), 3.75 (s, 2H, CH$_2$), 3.95 (q, 2H, CH$_2$O), 6.70(4H, ABq), 7.20–7.50 (gr. sign. 5H$_{arom.}$), 13.8 (bs, 1H,NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	14.6 (CH$_3$), 30.50 (ArCH$_2$), 62.9 (CH$_2$O), 114.2, 128.24, 129.2, 129.4, 129.6 (CH), 126.1, 133.6,151.5, 157.4(qC), 167.8 (C=S).
4k	IR-spectrum[λ_{max}/cm^{-1}]:	1510 (C=N); 1300 (C=S);
	UV[EtOH, λ/nm]:	228; 254; 284;
	^{1}H NMR [DMSO-d$_6$, ppm]:	0.77 (t, 3H, CH$_3$Bu), 1.17–1.22 (m, 4H, 2XCH$_2$), 1.28(t, 3H, CH$_3$, OEt), 3.78 (t, 2H, CH$_2$-1), 3.97(q, 2H, CH$_2$O), 4.02 (s, 2H, ArCH$_2$), 6.87 and 7.15(2d, 4H$_{arom.}$), 13.55(bs, 1H, NH);
	^{13}C NMR [DMSO-d$_6$, ppm]:	13.42 (CH$_3$), 14.56 (CH$_3$, EtO), 19.37, 29.3, 42.94 (3XCH$_2$-Bu), 30.04(ArCH$_2$), 62.9(CH$_2$,EtO), 114.6,(2XCH), 129.7(2XCH), 126.6,151.4,157.6 (qC), 166.67 (C=S).

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Резиме

СИНТЕЗА НА НЕКОИ НОВИ 4,5-ДИСУПСТИТУИРАНИ-2,4-ДИХИДРО--3Н-1,2,4-ТРИАЗОЛИН-3-ТИОНИ

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Клучни зборови: супституирани бензоил/фенацетил хидразини; супституирани бензоил/фенацетил-4-алкил/фенил тиосемикарбазиди; 1,2,4-триазолин-3-тиони

Со оксидативна циклизација на соодветни 2-, 3-, 4-хидроксибензоил-, 2-хидрокси-5-хлорбензоил-, 3,4,5-триметоксибензоил- и 4-хидрокси и 4-етоксифенацетил-4-$_M$-бутил/фенилтиосемикарбазиди се синтетизирани поголем број на 4,5-дисупстituирани-2,4-дихидро-3Н-1,2,4-триазолин-3-тиони (шема 1). Нивната структура е дискутирана врз основа на UV, IR, ^{1}H NMR и ^{13}C NMR спектрални податоци.