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SELECTIVE ALKYLATION OF AMINOMERCAPTO-1,2,4-TRIAZOLES: SYNTHESIS OF AMINONITRILES AND MERCAPTONITRILES

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2-or 3-cyanoalkyl-4-amino-5-aryl-1,2,4-triazoles were synthesized by condensing several 3-mercapto-4-amino-5-aryl-1,2,4-triazoles with halonitriles $Cl(CH2)_nCN$ where n=1-3. These reactions afforded new compounds and the use of different bases aids in accomplishing exclusive N or S alkylation at 2 or 3 position of the triazoles.

Keywords: 3-mercapto-4 -amino-5-aryl-1,2,4-triazoles; 1,2,4-triazole derivatives; halonitriles; S-H and N-H tautomers

INTRODUCTION

The important biological activity of mercapto amino-1,2,4-triazoles combined with some interesting synthesis problems have initiated a variety of research projects[1,2,3]. In our ongoing research for heterocycles containing vicinal amino and mercapto groups[4], we now report an example of reactivity of halonitriles $Cl(CH_2)_n$ CN toward the positions −2 or −3 of several tautomeric (S-H/N-H) 3-mercapto-4-amino-1,2,4-triazoles **1**.

The literature provides only scanty reactions on the tautomeric thione/thiol forms of compounds **1**; as far as we know there have been only few reports[5].

So we wish to report that, by using a wide range of reaction conditions, the 3-thiol/thione of compounds **1** reacts with halonitriles (n=1,2,3) to the

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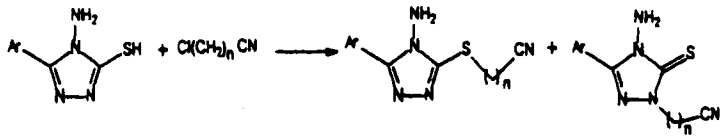
thiol form (S-3) or to the potentially tautomeric ring (NH-2), masking either the amino or the mercapto group, one at a time. This paper describes the possibility of synthesizing new aminonitriles and/or mercaptonitriles with the same n value. A pathway similar to the one developed for the synthesis of nitriles when n=2 was applied to compounds **1**. The triazoles reacted in a Michael-type fashion with acrylonitrile.

These methods illustrate the alkylation of ambident anions derived from aminomercapto triazoles and represents a novel approach to a series of nitriles which form a promising class of compounds with synthetic potentials.

RESULTS AND DISCUSSION

A group of four 1,2,4-triazoles **1** (scheme 1) were prepared by hydrazinolysis of the corresponding potassium-3-aroyldithiocarbazates with excess hydrazine hydrate following the Reid and Heindel procedure[6].



1a-d **2,3,4** **5,6,7**

	n=1 N°	n=2 N°	n=3 N°	n=1 N°	n=2 N°	n=3 N°
1a Ar : C_6H_5	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
1b Ar : CH_2-C_6H_5	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**
1c Ar : p.CH_3-C_6H_4	**2c**	**3c**	**4c**	**5c**	**6c**	**7c**
1d Ar : p.Cl-C_6H_4	**2d**	**3d**	**4d**	**5d**	**6d**	**7d**

SCHEME 1

We compared the reactivity of halonitriles on compounds **1a-d** with n values = 1,2,3. The influence of the halonitrile/ base ratio was also investigated.

TABLE I Aminonitriles and mercaptonitriles 2–7 with routes i and ii

Entry	Comp	Method[a]	n=1			n=2			n=3		
			Relative yield %	Relative yield %	Isolate yield %	Relative yield %	Relative yield %	Isolate yield%	Relative yield %	Relative yield %	Isolate yield%
1	**1a**	i	**2a** 100	**5a** 0	65	**3a** 0	**6a** 100	20	**4a** 100	**7a** 0	25
		ii	65	35	20	0	100	78	55	45	46
2	**1b**	i	**2b** 100	**5b** 0	47	**3b** 0	**6b** 100	20	**4b** 100	**7b** 0	50
		ii	80	20	30	0	100	15	65	35	30
3	**1c**	i	**2c** 100	**5c** 0	55	**3c** 0	**6c** 100	50	**4c** 100	**7c** 0	35
		ii	70	30	32	0	100	20	70	30	20
4	**1d**	i	**2d** 100	**5d** 0	51	**3d** 0	**6d** 100	60	**4d** 100	**7d** 0	60
		ii	60	40	35	0	100	60	50	50	50

a. key: (method i): triazoles **1a-d** (0,01 mol), halogenonitriles (0.04 mol), Et_3N (0.006 mol), ethanol. (method ii): triazoles **1a-d** (0.01 mol), halogenonitriles (0.012 mol), K_2CO_3 (0.02 mol), acetone.

Experimental part gives a description of the synthetic strategy used for the preparation of nitriles **2–7**. In a typical experiment **1a-d** (1 eq.) were heated under reflux in the presence of halonitriles/Et_3N: (4 eq/0.6eq) in ethanol (method i) or with halonitriles/K_2CO_3: (1.2eq/2 eq) in acetone at reflux (method ii).

Eweiss and Coll. [7]prepared compounds **2** (for example **2a** with a 56% yield) in boiling ethanol with an excess of chloroacetonitrile. Since spectroscopic data (^1H) were given, we repeated the synthesis with routes i (table I) and we were able to confirm the nitrile structure **2a** by NMR spectroscopy ^1H and ^{13}C. However, under our modified conditions (presence of Et_3N in route i) the reaction provided a 65% nitrile yield.

The results obtained under our two experimental conditions (for comparisons) are given in Table I.

The reactions were monitored by TLC. The products were purified by column chromatography on silica gel and identified from their analytical and spectral data. All compounds were investigated by ^1H, ^{13}C NMR and IRFT spectra.

When the results obtained with n=2 were compared with those obtained with n=1 or n=3, the first difference observed was that with n=2 no product **3a-d** resulting from the formation of a mercaptonitrile could be isolated either with Et_3N or in the presence of K_2CO_3. Compounds **6a-d** (aminonitriles) were the only isolated products generally with fairly yields.

The second observation that is worth noting is that using the same reaction conditions, similar results were obtained in the cases of n=1 and n=3.

– In the presence of K_2CO_3 (method ii) the substitution of the sulfur atom competes with the substitution of the nitrogen atom; triazoles **1b-d** reacted with chloronitriles in an manner analogous to that of **1a**.Two isomers were isolated, one with the nitrile chain on the N-2 of the triazole ring (compounds **5a-d** and **7a-d**) and the other with this chain attached to the triazole sulfur (products **2a-d** and **4a-d**). The results in Table I show that the reaction mixture after work-up afforded mercaptonitriles predominantly (entry 1: for n=1 **2a/5a** in a 65: 35 ratio, and for n=3 **4a/7a** in a 55: 45 ratio). To attempt to modify this ratio for example when n=3, the reaction carried out under the same conditions (chlorobutyronitrile (1,2 eq), K_2CO_3 (2eq)) but in the presence of ethanol afforded **4a** in higher yields (**4a/7a** in a 96: 4 ratio). The global reaction yield remained the same (45%).

We can note that the ratio of N-2 versus S-3 substitution of triazoles **1** does not depend on the properties of phenyl substituents at C-5 i.e. electron-donating (R=CH_3, entry 3) or electron-withdrawing (R=Cl, entry 4) groups.

– When Et_3N (method **i**) was used instead of K_2CO_3 only one isomer was obtained (100% of mercaptonitriles **2** for n=1 or **4** for n=3 but no aminonitriles, respectively **5** (n=1) or **7**(n=3), were detected. The selectivity may be due to the lower basicity of Et_3N with respect to K_2CO_3 i.e. their relative nucleophilicity.

Considering the above results, the best reaction conditions for synthesis of aminonitriles where n=1 or n= 3 (type **5** or **7**) implies using 1.2 mmol of chloronitriles, 2 mmol of K_2CO_3 as base in acetone with 1 mmol of triazoles **1** (method ii).

Then, the conditions of reaction between **1a** and halonitriles when n=2 were changed to find out if mercaptonitriles type **3a-d** could be obtained by changing factors such as solvent, nature of the halonitrile or temperature. Relevant results are presented in Table II.

TABLE II Reactions between **1a** and halonitriles ($X(CH2)_nCN$) when n=2

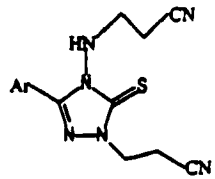
Entry	*Halonitrile*	*Conditions, time*	*Relative yield*		*Isolate yield*
1	$Cl(CH_2)_2CN$	Et_3N or K_2CO_3 (0.3 mmol), CH_3CN	100%	**6a**	30%
	1 mmol	12h reflux			
2	$Cl(CH_2)_2CN$/ $Na_2S_2O_4$	K_2CO_3 (2 mmol), EtOH/H_2O (50/50)	100%	**3a**	25%
	1 mmol	12h reflux			
3	$Br(CH_2)_2CN$	Et_3N (0.3 mmol), C_2H_5OH	40%	**3a**	30%
	1,2 mmol	12h reflux	60% ethylester of **3a**		

– Using another polar solvent (acetonitrile) and increasing the temperature with Et_3N or K_2CO_3 did not change the result (entry 1).

– Adding sodium dithionite at room temperature and leaving the mixture to boil for 12h in ethanol/water (ratio 1/1) did not improve the result either.

Finally, the first substantial improvement was obtained by using *bromo*propionitrile (entry 3) but still the yield of mercaptonitrile **3a** was only 40% (the major component-60%- corresponding to esterification of the CN group).

TABLE III Michael addition with compounds **1** (5 mmol) acrylonitrile (6 mmol), K_2CO_3 (5 mmol) in CH_3CN (15 ml) at 50°C



Ar: $CH_2C_6H_5$: **8b**
Ar: p.$CH_3C_6H_5$: **8c**

Entry/Comp. N°	*Time*	*Products N°*	*Isolate yield (%)*
1/**1a**	15 h	**6a**	51
2/**1b**	5 h	**8b**	33
3/**1c**	5 h	**8c**	22
4/**1d**	7 h	**6d**	20

Although preparation of mercaptopropionitriles **3** was possible by this route, the method was not sufficiently efficient to be investigated further.

For all structures **2 –7**, infrared spectra retained a peak about 2200 cm^{-1} (ν**CN** stretching vibrations) and the characteristic primary amine (N-**NH2** in 4 position) bands about 3300 cm^{-1}. ^1H RMN spectra displayed a singlet, D_2O exchangeable and integrated for 2 protons (N-**NH2**) at about δ 5.9 ppm which excludes adduct formation involving the primary amino-group and the nitrile.

^1H and ^{13}C NMR data (Table IV) provided support for existence of isomerism between mercaptonitriles **2a-d, (3a** or **4a-d)** and aminonitriles **5a-d (6a-d** or **7a-d)**.

For example (Table IV) examination of mercaptonitriles and aminonitriles indicates:

- for **S-CH2**- in **2a** an upfield shift of 0.6 ppm (NMR ^1H) and about 18 ppm (NMR ^{13}C) in comparison to **N-CH2**- in **5a**.
- a notable difference in the ^{13}C chemical shifts of C3 in the triazole ring, this confirms that aminonitriles **5** (**6** or **7**) exist preferably in the thione C=S function near δ: 167 ppm rather than the thiol form C-SH near δ: 155 ppm in mercaptonitriles **2** (**3a** or **4**). As expected, the C_3 carbon undergoes the strongest chemical shift change (ca 12 ppm) a downfield shift when going from compounds **2** to **5** for example as a result of the re-hybridation of C_3 from sp3 to sp2. Another remarkable shift is displayed by C_5which resonates at a lower frequency in aminonitriles (149 ppm in **6a**, 154.2 ppm in **3a** for example).

TABLE IV NMR ^{1}H and ^{13}C of compounds **2a-d – 7a-d**

	n=1				*n=2*				*n=3*			
	S-CH$_2$-CN Products N° 2		*N-CH$_2$-CN Products N° 5*		*S-(CH$_2$)$_2$-CN Products N° 3*		*N-(CH$_2$)$_2$-CN Products N° 6*		*S-(CH$_2$)$_3$-CN Products N° 4*		*N-(CH$_2$)$_3$-CN Products N° 7*	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
a	4.35	16.3/117.6	3.75	34.6/118	3.10 3.45	17.9 26.7/119	3.15 4.45	16.1 44.6/118	2.05 2.65 3.25	15.3 25.0 29.9/120	2.1 2.6 4.3	13.9 23.7 46.2/119.8
b	4.35	16.5/117	3.6	35.2/118.0			3.05 4.35	15.99 44.27/118	2.08 2.68 3.35	15.6 25.0 29.9/123.0	2.15 2.65 4.32	13.9 24.8 46.8/119.5
c	4.4	16.5/117.6	3.8	34.3/117.0			3.14 4.45	16.05 44.55/118	2.05 2.75 3.35	15.2 25.3 29.9/121	2.18 2.6 4.3	13.7 23.8 46.2/117.7
d	4.43	16.49/117.6	3.75	34.5/117.7			3.15 4.44	16.07 44.66/118.1	2.10 2.68 3.25	16.3 25.5 29.4/120.1	2.2 2.57 4.25	13.3 23.2 45.2/119.3

A potentially interesting alternative to obtain compounds **3** would to be use a Michael addition. So, we therefore decided to introduce the cyanide group through acrylonitrile and K_2CO_3 in acetonitrile at 50°C (entries 1–3, Table III). With regard to halonitrile reaction, this Michael addition proceeded in good yields to afford only N substituted nitriles: monosubstituted **6a** or **6d** with triazoles **1a** and **1d**. With isomers **1b** and **1c** compounds **8b** and **8c** (Table III) identified as N disubstituted adducts were isolated only in the presence of an electron-donating group on the phenyl ring.

These results indicate that compounds **1** reacted with the thione form under Michael conditions. This is in agreement with studies of Kovalev and Coll.[5] who have reported that the 3-thiol/thione form of 3(3H)-1,2,4-triazole-thione adds to acrylonitrile preferably to the potentially tautomeric ring NH; however, Rani and coll.[8] have indicated that Michael addition of compounds type **1** with o-benzoquinone occurred through the thiol group.

The NMR spectra of **8** or **9** lacked the characteristic of the NH_2 of the hydrazide group (near 6 ppm), and exhibited a pattern in accordance with the structure assigned. Absence of NH-2 near 13 ppm, and presence of four methylene groups (ex for **8b**: 4H t, $\delta = 3 - 4.3$ ppm N-$(CH_2)_2$ and 4H m δ =2.6–3.3 ppm for $(CH_2)_2$ on NH hydrazino.

In conclusion, this work provides a general methodology for the introduction of alkylnitriles through N-H or S-H group of diversely 5-susbtituted-4-amino-3-mercapto-1,2,4-triazoles; moreover, the simplicity of the reaction could suggest a possible application of this methodology for generating combinatorial 2- or 3- substituted amino-mercapto triazoles [(9)]. It is worth noting that this reaction, which is the first step to an easy synthesis of other compounds, could be used to test the antimicrobial and fungicidal activities of our products.

EXPERIMENTAL

The IR spectra were recorded on a 16PC FTIR Perkin-Spectrometer. Solids were examined with a diffuse reflectance accessory. ^1H NMR and ^{13}C NMR spectra were recorded using TMS as the internal standard; chemical shifts were in ppm. Compounds were purified by column chromatography

with silicagel 60 (70–230 mesh) purchased from Merck. Meltings points were determined on a Kofler melting point apparatus and are uncorrected. Solids were recristallised in EtOH.

Synthesis of 5- aryl-4amino-3-mercapto-1,2,4-triazoles 1

These compounds were prepared according to the method reported by Reid and Coll.[6]

General procedure i

A mixture of triazoles **1a-d** (0.01 mol), chloroacetonitrile (0.04 mol) and triethylamine (0.006 mol) in 30ml absolute ethanol was gently refluxed for 2–12 hours until the triazole was consumed; the reaction was monitored by TLC. The mixture was concentrated under reduce pressure and the residue was treated with water (25 ml) and neutralized by Na_2CO_3. A precipitate was formed, washed with cold water and collected by filtration. The product was purified by column chromatography (CC) on silicagel (or was recrystallized from absolute ethanol to give analytically pure samples).

General procedure ii

A mixture of triazole **1a-d** (0.01 mol), CO_3K_2(0.02 mol) and chloroacetonitrile (0.012 mol) in 30 ml acetone was heated at reflux until the triazole was consumed (reaction monitored by TLC). The mixture was concentrated under reduce pressure, the residue was treated with cold water (25 ml). The compound was collected by filtration, washed with cold water (3x15 ml). The product was subjected to column chromatography (CC) on silicagel.

(2a): (4-amino-5-phenyl-4H-1,2,4-triazol-3-ylsulphanyl)-methylenenitrile

m.p. 160°C[(7)]. IR (KBr): νNH_2: 3252 et 3126 cm^{-1}; νCN: 2246 cm^{-1}; νC=N: 1628 cm^{-1}. RMN ^{1}H: δ=4.35 ppm, s, 2H (CH_2); δ=6.30 ppm, s, 2H (NH_2); δ=7.55 ppm, m, 3H (*m*- et *p*-Ph); δ=8.00 ppm, m, 2H (*o*-Ph)

RMN ^{13}C: δ=16.3 ppm, t, J=152Hz (CH_2); δ=117.6 ppm, m (CN); δ=126.4 ppm, t, J=7Hz (*i*-Ph); δ=127.7 ppm, d, J=162Hz (*o*-Ph); δ=128.5 ppm, d, J=161Hz (*m*-Ph); δ=129.8 ppm, t, J=7Hz (*p*-Ph); δ=151.4 ppm, s (C-Ph); δ=154.6 ppm, s (C-S)

(2b): (4-amino-5-benzyl-4H-1,2,4-triazol-3-ylsulphanyl)-methylenenitrile

m.p. 130°C[7]. IR (KBr): νNH_2: 3252 et 3193 cm^{-1}; νCN: 2254 cm^{-1}; νC=N: 1621 cm^{-1}. RMN ^1H: δ = 4.03 ppm, s, 2H (CH_2-C_6H_5); δ = 4.35 ppm, s, 2H (CH_2); δ = 5.55 ppm, s, 2H (NH_2); δ = 7.55 ppm, m, 3H (*m*- et *p*-Ph); δ = 8.00 ppm, m, 2H (*o*-Ph)

RMN ^{13}C: δ = 16.5 ppm, t, J = 152Hz (CH_2); δ = 31.08 ppm, t, J = 131Hz (CH_2-Ph); δ = 117 ppm, m (CN); δ = 127.7 ppm, t, J = 161Hz (*p*-Ph); δ = 129.4 ppm, d, J = 160Hz (*m*-Ph);

δ = 129.7 ppm, d, J = 159Hz (*o*-Ph); δ = 136.3 ppm, m (*i*-Ph); δ = 151.4 ppm, s (C-Ph); δ = 154.6 ppm, s (C-S).

(2c): (4-amino-5-*p*-methylphenyl-4H-1,2,4-triazol-3-ylsulphanyl)-methylene nitrile

m.p. 184°C[7]. IR (KBr): νNH_2: 3242 et 3120 cm^{-1}; νCN: 2256 cm^{-1}; νC=N: 1628 cm^{-1}. RMN ^1H: δ = 2.45 ppm s, 3H (CH_3), δ = 4.4 ppm, s, 2H (CH_2); δ = 6.40 ppm, s, 2H (NH_2); δ = 7,60 – 7.70 ppm, d, 2H (*m*-, *o*-Ph); δ = 8,12 – 8.15 ppm, d, 2H (*m*- et *o*-Ph)

RMN ^{13}C: δ = 16.5 ppm, t, J = 153Hz (CH_2) δ = 20.95 ppm, qt, J = 127Hz (CH_3); δ = 117.6 ppm, m (CN); δ = 124.36 ppm, t, J = 8.5Hz (*p*-Ph); δ = 129 ppm, dd, ^1J = 158Hz (*m*-Ph); δ = 129.62 ppm, dd, ^1J = 160Hz (*o*-Ph); δ = 134.71 ppm, s (*ipso*-Ph); δ = 151.52 ppm, s (C-Ph); δ = 154.77 ppm, s (C-S).

(2d): (4-amino-5-*p*-chlorophenyl-4H-1,2,4-triazol-3-ylsulphanyl)-methylene nitrile

m.p. 154°C[7]. IR (KBr): νNH_2: 3252 et 3126 cm^{-1}; νCN: 2246 cm^{-1}; νC=N: 1628 cm^{-1}. RMN ^1H: δ = 4.43 ppm, s, 2H (CH_2); δ = 6.39 ppm, s,

2H (NH_2); δ = 7.70 – 7.73 ppm, d, 2H (*m*- – *o*-Ph); δ = 8.12 – 8.15 ppm, d, 2H (*m*- et *o*-Ph)

RMN ^{13}C: δ = 16.49 ppm, t, J = 152Hz (CH_2); δ = 117.6 ppm, m (CN); δ = 125.36 ppm, t, J = 8,5Hz (*p*-Ph); δ = 128.68 ppm, dd, ^1J = 160Hz (*m*-Ph); δ = 129.42 ppm, dd, ^1J = 159Hz (*o*-Ph); δ = 134.71 ppm, s (*ipso*-Ph); δ = 151.72 ppm, s (C-Ph); δ = 153.77 ppm, s (C-S)

(5a): 4-amino-5-phenyl-2-méthylènenitrile-2,4-dihydro-1,2,4-triazole-3-thione

oil. CC: $CHCl_3$/AcOEt 95/5. IR (KBr): νNH_2: 3364 et 3186 cm^{-1}; νCN: 2196 cm^{-1}; νC=N: 1654 cm^{-1}

RMN ^1H: δ=3.75 ppm, s, 2H (CH_2-CN); δ=7.20 ppm, s, 2H (NH_2); δ=7.50 ppm, m, 3H (*m*- et *p*-Ph); δ=8.10 ppm, m, 2H (*o*-Ph)

RMN ^{13}C: δ = 34.6 ppm (CH_2); δ = 118 ppm, m (CN); 8=126.7 ppm, t, J=7Hz (*i*-Ph); δ=127.9 ppm, d, J=162Hz (*o*-Ph); δ=128.8 ppm, d, J=161Hz (*m*-Ph); δ=130 ppm, t, J=7Hz (*p*-Ph); δ=151.4 ppm, s (C-Ph); δ=167 ppm, s (C=S)

(5b): 4-amino-5-benzyle-2-methylenenitrile-2,4-dihydro-1,2,4-triazole-3-thione

oil. CC: $CHCl_3$/AcOEt 95/5. IR (KBr): νNH_2: 3360 et 3186 cm^{-1}; νCN: 2200 cm^{-1}; νC=N: 1655 cm^{-1}

RMN ^1H: δ=3.6 ppm, s, 2H (CH_2 -CN); δ=4.11 ppm, s, 2H (CH_2-C_6H_5) δ=7.20 ppm, s, 2H (NH_2); δ=7.60 ppm, m, 2H; δ=8.10 ppm, m, 2H.

RMN ^{13}C: δ=35.2 ppm, t, (CH_2-C_6H_5) δ=44.3 ppm, t, (CH_2-CN); δ=118 ppm, m (CN); δ=126.8 ppm, t, J=7Hz (*i*-Ph); δ=127.7 ppm, d, J=162Hz (*o*-Ph); δ=128.5 ppm, d, J=161Hz (*m*-Ph); δ=126.8 ppm, q, (*p*-Ph); δ=152.4 ppm, s (C-Ph); δ=166.6 ppm, s (C=S).

(5c): 4-amino-5-methyl-2-methylenenitrile-2,4-dihydro-1,2,4-triazole-3-thione

oil. CC: $CHCl_3$/AcOEt 95/5. IR (KBr): νNH_2: 3360 et 3140 cm^{-1}; νCN: 2210 cm^{-1}; νC=N: 1664 cm^{-1}

RMN ^{1}H: $\delta = 2.45$ ppm s, 3H (CH_3) δ=3.8 ppm, s, 2H (CH_2 -CN); δ=7.30 ppm, s, 2H (NH_2); δ=7.50 ppm, m, 2H; δ=8.20 ppm, m, 2H.

RMN ^{13}C: δ=34.3 ppm, t, (CH_3), δ=43.3 ppm, t, (CH_2-CN); δ=117 ppm, m (CN); δ=127.8 ppm, t, J=7Hz (*i*-Ph); δ=127.9 ppm, d, J=162Hz (*o*-Ph); δ=128.7 ppm, d, J=161Hz (*m*-Ph); δ=151.8 s (C-Ph); δ=166.6 ppm, s (C=S)

(5d): (4-amino-5-*p*-chlorophenyl-4H-1,2,4-triazol-3-ylsulphanyl)-methylene nitrile

oil. CC: $CHCl_3$/AcOEt 95/5. IR (KBr): νNH_2: 3262 et 3129 cm^{-1}; νCN: 2256 cm^{-1}; νC=N: 1618 cm^{-1}

RMN ^{1}H: $\delta = 3.75$ ppm, s, 2H (CH_2); $\delta = 6.34$ ppm, s, 2H (NH_2); $\delta = 7.75 - 7.83$ ppm, d, 2H (Ph); $\delta = 8.15 - 8.25$ ppm, d, 2H (Ph)

RMN ^{13}C: $\delta = 34.5$ ppm, t, J = 152Hz (CH_2); $\delta = 117.7$ ppm, m (CN); $\delta = 129.68$ ppm, dd, ^{1}J = 160Hz (*m*-Ph); $\delta = 129.42$ ppm, dd, ^{1}J = 159Hz (*o*-Ph); $\delta = 134.77$ ppm, s (*ipso*-Ph); $\delta = 151$ ppm, s (C-Ph); $\delta = 166.8$ ppm, s (C=S)

(3a): 4-amino-5-phenyl-4H-1,2,4-triazol-3-ylsulphanyl)-3-propionitrile

m.p. 98°C. CC: AcOET/MeOH/Et_3N 80/10/10. IR (KBr): νNH_2: 3364, 3262 et 3192 cm^{-1}; νCN: 2252 cm^{-1}; νC=N: 1622 cm^{-1}

RMN ^{1}H: δ=3.10 ppm, t (J=6.7Hz), 2H (CH_2-CN); δ=3.45ppm, t (J=6.7Hz), 2H (CH_2-S); δ=6.20 ppm, s, 2H (NH_2); δ=7.55 ppm, m, 3H (*m*- et *p*-Ph); δ=8.00 ppm, m, 2H (*o*-Ph) RMN ^{13}C; δ=17.9 ppm, t, J=137.7 ppm (C-CN); δ=26.7 ppm, t, J=145.7 ppm (CH_2-S); δ=119.0 ppm, m (CN); δ=126.7 ppm, t (*i*-Ph); δ=127.7 ppm, dt, J=162Hz (*o*-Ph); δ=128.4 ppm, dd, J=161Hz (*m*-Ph); δ=129.6 ppm, dt, J=162Hz (*p*-Ph); δ=152.5 ppm, t, J=5.6Hz (C-Ph); δ=154.2 ppm, t, J=3.2Hz (C-S)

(6a): 4-amino-5-phenyl-2-(3-propionitrile)-2,4-dihydro-1,2,4-triazole-3-thione

m.p. 114°C. CC: AcOET/MeOH/Et_3N 80/10/10. IR (KBr): νNH_2: 3302 et 3260 cm^{-1}; νCN: 2252 cm^{-1};νC=N: 1620 cm^{-1}

RMN ^{1}H: δ=3.15 ppm, t (J=6.4Hz), 2H (CH_2-CN); δ=4.45 ppm, t (J=6.4Hz), 2H (CH_2-N); δ=5.95 ppm, s, 2H (NH_2); δ=7.55 ppm, m, 3H (*m*- et *p*-Ph); δ=8.05 ppm, m, 2H (*o*-Ph)

RMN ^{13}C: δ=16.1 ppm, tt, J=138Hz et 3Hz (C-CN); δ=44.6 ppm, tt, J=147Hz et 5Hz (CH_2-N); δ=118.0 ppm, m (CN); δ=125.0 ppm, t, J=7.4Hz (*i*-Ph); δ=128.2 ppm, dt, J=165Hz (*o*-Ph); δ=128.5 ppm, dd, J=164Hz (*m*-Ph); δ=130.7 ppm, dt, J=162Hz (*p*-Ph); δ=149.0 ppm, m, J=2.2Hz (C-Ph); δ=166.8 ppm, t, J=3Hz (C=S).

(6b): 4-amino-5-benzyl-2-(3-propionitrile)-2,4-dihydro-1,2,4-triazole-3-thione

oil. CC: AcOET/MeOH/Et_3N 80/10/10. IR (KBr): νNH_2: 3302 et 3260 cm^{-1}; νCN: 2252 cm^{-1}; νC=N: 1620 cm^{-1}

RMN ^{1}H: δ=3.05 ppm, t (J=6.5Hz), 2H (CH_2-CN); δ=4.11 ppm, s (J=6.4Hz), 2H (CH_2-C6H5); δ=4.35 ppm, s, 2H (CH_2-N); δ=5.71 ppm, s, 2H, (NH2), δ=7.31 ppm, m, 5H (Ph)

RMN ^{13}C: δ=15.99 ppm, tt, J=138Hz (CH_2-CN); δ=30.6 ppm, t, J=147Hz (CH_2-C_6H_5) δ=44.27 ppm, tt, J=147Hz (CH_2-N); δ=118.0 ppm, m (CN); δ=126.8 ppm, t, (p-Ph); δ=128.4 ppm, dt, J=165Hz (*m*-Ph); δ=128.7 ppm, dd, J=164Hz (*o*-Ph); δ=135.06 ppm, dt, J=162Hz (*i*-Ph); δ=151.0 ppm, m, J=2.2Hz (C-Ph); δ=166 ppm, t, (C=S).

(6c): 4-amino-5-p methyl phenyl-2-(3-propionitrile)-2,4-dihydro-1,2,4-triazole-3-thione

oil. CC: AcOET/MeOH/Et_3N 80/10/10. IR (KBr): νNH_2: 3310 et 3256 cm^{-1}; νCN: 2250 cm^{-1}; νC=N: 1630 cm^{-1}

RMN ^{1}H: δ = 2.47 ppm s, 3H (CH_3),δ=3.14 ppm, t (J=6.4Hz), 2H (CH_2-CN); δ=4.45 ppm, t (J=6.5Hz), 2H (CH_2-N); δ=5.98 ppm, s, 2H (NH_2); δ=7.57 ppm, m, 2H (Ph); δ=8.05 ppm, m, 2H (Ph)

RMN ^{13}C: δ=16.05 ppm, tt, J=138Hz (CH_2-CN); δ=20,95 ppm, q, J=127Hz, 3H, (CH_3-C_6H_5), δ=44.55 ppm, tt, J=147Hz (CH_2-N); δ=118.0 ppm, m (CN); δ=122.2 ppm, t, J=7.4Hz (*i*-Ph); δ=128.1 ppm, dd, J=163Hz (*o*-Ph); δ=129 ppm, dm, J=164Hz (*m*-Ph); δ=149.0 ppm, m, J=2.2Hz (C-Ph); δ=166.6 ppm, t, J=3Hz (C=S).

(6d): 4-amino-5-p chlorophenyl-2-(3-propionitrile)-2,4-dihydro-1,2,4-triazole-3-thione

oil. CC: AcOET/MeOH/Et_3N 80/10/10. IR (KBr): νNH_2: 3315 et 3258 cm^{-1}; νCN: 2248 cm^{-1}; $\nu C{=}N$: 1630 cm^{-1}

RMN ^1H: $\delta = 2.47$ ppm s, 3H (CH_3), δ=3.15 ppm, t (J=6.2Hz), 2H (CH_2-CN); δ=4.44 ppm, t (J=6.2 Hz), 2H (CH_2-N); δ=5.88 ppm, s, 2H (NH_2); δ=7.59 ppm, d, 2H (m.Ph); δ=8.04 ppm, m, 2H (o.Ph)

RMN ^{13}C: δ=16.07 ppm, tt, J=138Hz (CH_2-CN); δ=44.66 ppm, tt, J=147Hz, 2H, (CH_2-N),; δ=118.1 ppm, m (CN); δ=128.7 ppm, dd, J=168 Hz (*m*-Ph); δ=129.9 ppm, dd, J=166Hz (*o*-Ph); δ=135.7 ppm, m,, J=10.8Hz (*i*-Ph); δ=148.1 ppm, s, (C-Ph); δ=167 ppm, t, (C=S).

4-amino-5-phenyl-2-(3-ethylpropionate)-2,4-dihydro-1,2,4-triazole-3-thione (ethylester of 3a)

oil. CC: CCl_4. IR (KBr): νNH_2: 3256 et 3134 cm^{-1}; $\nu C{=}O$: 1732 cm^{-1}; $\nu C{=}N$: 1650^{-1} RMN ^1H; δ=1.20 ppm, t (J=7Hz), 3H (CH_3); δ=2.85 ppm, t (J=7Hz), 2H (CH_2-C=O); δ=3.35 ppm, t, 2H (CH_2-S); δ=4.10 ppm, q (J=7Hz), 2H (CH_2-O); δ=6.10ppm, s, 2H (NH_2); δ=7.50 ppm, m, 3H (*m*- et *p*-Ph); δ=8.00 ppm, m, 2H (*o*-Ph)

RMN ^{13}C: δ=14.0 ppm, qt, J=127Hz (CH_3); δ=26.2 ppm, tt, J=144Hz (CH_2-S); δ=34.0 ppm, tt, J=131Hz (CH_2-C=O); δ=60.2 ppm, tq, J=148Hz (CH_2-O); δ=126.8 ppm, t, J=7Hz (*i*-Ph); δ=127.7 ppm, dt, J=162Hz (*o*-Ph); δ=128.4 ppm, dd, J=161Hz (*m*-Ph); δ=129.6 ppm, dt, J=161Hz (*p*-Ph); δ=153.1 ppm, t, J=5.5Hz (C-Ph); δ=154.1 ppm, t (C=S); δ=171.2 ppm, m (C=O)

(4a): (4-amino-5-phenyl-4H-1,2,4-triazol-3-ylsulphanyl)-4-butyronitrile

m.p. 124°C. CC: acetone/CCl_4 50/50. IR (KBr): νNH_2: 3330 et 3190 cm^{-1}; νCN: 2246 cm^{-1}; $\nu C{=}N$: 1624 cm^{-1}

RMN ^1H: δ=2.05 ppm, m (J=7.2Hz), 2H (C-CH_2-C); δ=2.65 ppm, t (J=7.2Hz), 2H (CH_2-CN); δ=3.25 ppm, t (J=7.2Hz), 2H (CH_2-S); δ=6.15 ppm, s, 2H (NH_2); δ=7.50 ppm, m, 3H (*m*- et *p*-Ph); δ=8.00 ppm, m, 2H (*o*-Ph)

RMN ^{13}: δ=15.3 ppm, tt, J=136Hz (C-CN); δ=25.0 ppm, tt, J=134Hz (CH_2-C-CH_2); δ=29.9 ppm, tt, J=142Hz (CH_2-S); δ=120.0 ppm, m (CN); δ=126.8 ppm, t, J=8Hz (i-Ph); δ=127.7 ppm, dt, J=162Hz (*o*-Ph); δ=128.4 ppm, dd, J=161Hz (*m*-Ph); δ=129.6 ppm, dt, J=162Hz (*p*-Ph); δ=152.9 ppm, t, J=5Hz (C-Ph); δ=154.1 ppm, s (C-S)

(4b): (4-amino-5-benzyl-4H-1,2,4-triazol-3-ylsulphanyl)-4-butyronitrile

oil. CC: acetone/CCl_4 50/50. IR (KBr): νNH_2: 3335 et 3190 cm^{-1}; νCN: 2240 cm^{-1}; νC=N: 1628 cm^{-1}

RMN ^{1}H: δ=2.08 ppm, m (J=7.2Hz), 2H (C-CH_2-C); δ=2.68 ppm, t (J=7.2Hz), 2H (CH_2-CN); δ=3.35 ppm, t (J=7.2Hz), 2H (CH_2-S); δ= 4,03 ppm, s, 2H (CH_2 -C_6H_5), δ=6.25 ppm, s, 2H (NH_2); δ=7.50 ppm, m, 3H (Ph); δ=8.10 ppm, m, 2H (Ph)

RMN^{13}: δ=15.6 ppm, tt, J=136Hz (C-CN); δ=25.0 ppm, tt, J=134Hz (CH_2-C-CH_2); δ=29.9 ppm, tt, J=142Hz (CH_2-S); δ = 31.08 ppm, t, J = 131Hz (CH_2-Ph), δ=123.0 ppm, m (CN); δ=127.8 ppm, t, J=8Hz (*i*-Ph); δ=127.7 ppm, dt, J=162Hz (*o*-Ph); δ=128.8 ppm, dd, J=161Hz (*m*-Ph); δ=129 ppm, dt, J=163Hz (*p*-Ph); δ=152.9 ppm, t, J=5Hz (C-Ph); δ=154.1 ppm, s (C-S)

(4c): (4-amino-5-p methylphenyl-4H-1,2,4-triazol-3-ylsulphanyl)-4-butyro nitrile

oil. CC: acetone/CCl_4 50/50. IR (KBr): νNH_2: 3329 et 3185 cm^{-1}; νCN: 2245 cm^{-1}; νC=N: 1624 cm^{-1}

RMN ^{1}H: δ = 2.47 ppm s, 3H (CH_3),δ=2.05 ppm, m (J=7.2Hz), 2H (C-CH_2-C); δ=2.75 ppm, t (J=7.2Hz), 2H (CH_2-CN); δ=3.35 ppm, t (J=7.2Hz), 2H (CH_2-S); δ=6.15 ppm, s, 2H (NH_2); δ=7.50 ppm, m, 2H (Ph); δ=8.00 ppm, m, 2H (Ph)

RMN^{13}: δ=15.2 ppm, tt, J=136Hz (C-CN); δ=25.3 ppm, tt, J=134Hz (CH_2-C-CH_2); δ=29.9 ppm, tt, J=142Hz (CH_2-S); δ=20.95 ppm, q, J=127Hz, 3H,(CH_3-C_6H_5), δ=121.0 ppm, m (CN); δ=127.8 ppm, t, J=8Hz (*i*-Ph); δ=128,3 ppm, dt, J=162Hz (*o*-Ph); δ=128.6 ppm, dd, J=161Hz (*m*-Ph), δ=153.9 ppm, t, J=5Hz (C-Ph); δ=154.3 ppm, s (C-S)

(4d): (4-amino-5-p.chlorophenyl-4H-1,2,4-triazol-3-ylsulphanyl)-4-butyro nitrile

semi-solid. CC: acetone/CCl_4 50/50. IR (KBr): νNH_2: 3330, 3195 cm^{-1}; νCN: 2248 cm^{-1}; $\nu C{=}N$: 1628 cm^{-1}

RMN ^1H: δ=2.10 ppm, m(5) (J=7.2Hz), 2H (C-CH_2-C); δ=2.68 ppm, t (J=7.2Hz), 2H (CH_2-CN); δ=3.25 ppm, t (J=7.2Hz), 2H (CH_2-S); δ=6.15 ppm, s, 2H (NH_2); δ=7.50 ppm, m, 2H (Ph); δ=8.00 ppm, m, 2H (Ph)

RMN ^{13}: δ=16.3 ppm, tt, J=136Hz (C-CN); δ=25.5 ppm, tt, J=134Hz (CH_2-C-CH_2); δ=29.4 ppm, tt, J=142Hz (CH_2-S); δ=120.1 ppm, m (CN); δ=126.8 ppm, t, J=8Hz (*i*-Ph); δ=127.9 ppm, dt, J=162Hz (*o*-Ph); δ=129.4 ppm, dd, J=161Hz (*m*-Ph); δ=152.0 ppm, t, J=5Hz (C-Ph); δ=154.3 ppm, s (C-S).

(7a): 4-amino-2-(4-butyronitrile)-5-phenyl-2,4-dihydro-1,2,4-triazole-3-thione

oil. CC: AcOET/MeOH/Et_3N 80/10/10. RMN ^1H: δ=2.10 ppm, m, (J=6.9Hz), 2H (C-CH_2-C); δ=2.60 ppm, t (J=7.2Hz), 2H (CH_2-CN); δ=4.30 ppm, t (6.7Hz), 2H (CH_2-N); δ=5.85 ppm, s, 2H (NH_2); δ=7.55 ppm, m, 3H (*m*- et *p*-Ph); δ=8.05 ppm, m, 2H (*o*-Ph)

RMN ^{13}C: δ=13.9 ppm, tt, J=134Hz et 4Hz (CH_2-CN); δ=23.7 ppm, tt, J=133Hz C-CH_2-C; δ=46.2 ppm, tt, J=142Hz (CH_2-N); δ=119.8 ppm, m (CN); δ=125.3 ppm, t, J=7Hz (*i*-Ph); δ=128.3 ppm, dt, J=163Hz et 7Hz (*o*-Ph); δ=128.4 ppm, dd, J=162Hz et 6Hz (*m*-Ph); δ=130.6 ppm, dt, J=162Hz (*p*-Ph); δ=148.8 ppm, s (C-Ph); δ=166.3 ppm, t (C=S)

(7b): 4-amino-2-(4-butyronitrile)-5-benzyl-2,4-dihydro-1,2,4-triazole-3-thione

oil. CC: AcOET/MeOH/Et_3N 80/10/10. RMN ^1H: δ=2.15 ppm, m, (J=6.9Hz), 2H (C-CH_2-C); δ=2.65 ppm, t (J=7.2Hz), 2H (CH_2-CN); δ=4.21 ppm, s (J=6.4Hz), 2H (CH_2-C_6H_5), δ=4.32 ppm, t (6.7Hz), 2H (CH_2-N); δ=5.90 ppm, s, 2H (NH_2); δ=7.75 ppm, m, 2H (Ph); δ=8.15 ppm, m, 2H (Ph)

RMN ^{13}C: δ=13.9 ppm, tt, J=134Hz (CH_2-CN); δ=24.8 ppm, tt, J=133Hz C-CH_2-C; δ = 31.18 ppm, t, J = 131Hz (CH_2-Ph), δ=46.8 ppm, tt, J=142Hz (CH_2-N); δ=119.5 ppm, m (CN); δ=125.3 ppm, t, J=7Hz

(*i*-Ph); δ=128.8 ppm, dt, J=163Hz et 7Hz (*o*-Ph); δ=128.6 ppm, dd, J=162Hz (*m*-Ph); δ=133.6 ppm, dt, J=162Hz et 8Hz (*p*-Ph); δ=149.8 ppm, s (C-Ph); δ=166.2 ppm, t (C=S).

(7c): 4-amino-2-(4-butyronitrile)-5-p.methylphényl-2,4-dihydro-1,2,4-triazole-3-thione

semi-solid. CC: AcOET/MeOH/Et_3N 80/10/10. RMN ^1H: δ=2.18 ppm, m, (J=6.9Hz), 2H (C-CH_2-C); δ = 2,42 ppm s, 3H (CH_3) δ=2.60 ppm, t (J=7.2Hz), 2H (CH_2-CN); δ=4.30 ppm, t (6.7Hz), 2H (CH_2-N); δ=5.80 ppm, s, 2H (NH_2); δ=7.54 ppm, m, 2H (Ph); δ=8.05 ppm, m, 2H (Ph)

RMN ^{13}C: δ=13.7 ppm, tt, J=134Hz (CH_2-CN); δ = 20.95 ppm, q, J = 127Hz (CH_3), δ=23.8 ppm, tt, J=133 Hz C-CH_2-C; δ=46.2 ppm, tt, J=142Hz (CH_2-N); δ=119.7 ppm, m (CN); δ=125.3 ppm, t, J=7 Hz (*i*-Ph); δ=128.5 ppm, dt, J=163Hz (*o*-Ph); δ=128.5 ppm, dd, J=162Hz et (*m*-Ph), δ=148.8 ppm, s (C-Ph); δ=166.8 ppm, t (C=S).

(7d): 4-amino-2-(4-butyronitrile)-5-p.chlorophenyl-2,4-dihydro-1,2,4-triazole-3-thione

oil. CC: AcOET/MeOH/Et_3N 80/10/10. RMN ^1H: δ=2.20 ppm, m, (J=6.7Hz), 2H (C-CH_2-C); δ=2.57 ppm, t (J=7.3Hz), 2H (CH_2-CN); δ=4.25 ppm, t (6.8Hz), 2H (CH_2-N); δ=5.83 ppm, s, 2H (NH_2); δ=7.95 ppm, m, 2H (Ph); δ=8.25 ppm, m, 2H (Ph)

RMN ^{13}C: δ=13.3 ppm, tt, J=136Hz (CH_2-CN); δ=23.2 ppm, tt, J=135Hz C-CH_2-C; δ=45.2 ppm, tt, J=141Hz (CH_2-N); δ=119.3 ppm, m (CN); δ=124.3 ppm, t, J=7Hz (*i*-Ph); δ=127.9 ppm, dt, J=162Hz (*o*-Ph); δ=128.8 ppm, dd, J=162Hz (*m*-Ph), δ=148.7 ppm, s (C-Ph); δ=166.0 ppm, t (C=S).

(8b) 5-benzyl-4(3-propionitrile)-amino-2(3-propionitrile)-2,4-dihydro-1,2,4-triazole-3-thione

m.p. CC: $CHCl_3$/AcOEt 95/5. 130°C. RMN ^1H: δ=2.65 ppm, t(J=6.0Hz), 2H (NH-CH_2-**CH_2**-CN); δ=3,04 ppm, t (J=6.3Hz), 2H (N-CH_2-**CH_2**-CN); δ=3.29 ppm, m (6.8Hz), 2H (NH-**CH_2**-CH_2-CN);

δ=4.12 ppm, s, 2H (CH_2-C_6H_5); δ=4.33 ppm, t, 2H (N-**CH_2**-CH_2-CN), δ=6.67 ppm, m, 1H (N-NH); δ=7.33 ppm, m, 5H (Ph)

RMN ^{13}C: δ=15.4 ppm, td, J=138Hz (NH-CH_2-**CH_2**-CN); δ=15.5 ppm, t, J=137Hz (N-CH_2-**CH_2**-CN); δ=29.1 ppm, t, J=131Hz (CH_2-C_6H_5); δ=43.4 ppm, t, J=146Hz (NH-**CH_2**-CH_2-CN); δ=43.6 ppm, t, J=143Hz (N-**CH_2**-CH_2-CN); δ=117.4 ppm, m, ($NH(CH_2)_2$**CN**); δ=118.9 ppm, m, ($N(CH_2)_2$**CN**), δ=126.4 ppm, d, J=160Hz (*p*-Ph), δ=127.9 ppm, d, J=160Hz (*m*-Ph), δ=128.2 ppm, d, J=160Hz (o-Ph), δ=134.3 ppm, m, (*i*-Ph), δ=150.9 ppm, m (C-Ph); δ=165.0 ppm, s (C=S).

(8c) 5-p methylphenyl-4(3-propionitrile)-amino-2(3-propionitrile)-2,4-dihydro-1,2,4-triazole-3-thione

m.p. 150°C. CC: $CHCl_3$/AcOEt 95/5. RMN ^1H: δ = 2.42 ppm s, 3H (CH_3), δ=2.57 ppm, t (J=6.5Hz), 2H (NH-CH_2-**CH_2**-CN); δ=3.11 ppm, t (J=6.5Hz), 2H (N-CH_2-**CH_2**-CN); δ=3.38 ppm, m (6.0Hz), 2H (NH-**CH_2**-CH_2-CN); δ=4.43 ppm, t, 2H (N-**CH_2** CH_2-CN); δ=6.81 ppm, t, 1H (N-NH); δ=7.35 ppm, d, 2H (m-Ph),; δ=7.97 ppm, d, 2H (o-Ph)

RMN ^{13}C: δ=15.5 ppm, td, J=138Hz (NH-CH_2-**CH_2**-CN); δ=16.5 ppm, t, J=137Hz (N-CH_2-**CH_2**-CN); δ=43.4 ppm, t, J=146Hz (NH-**CH_2**-CH_2-CN); δ=45.6 ppm, t, J=143Hz (N-**CH_2**-CH_2-CN); δ=117.6 ppm, m, ($NH(CH_2)_2$**CN**); δ=118.7 ppm, m, ($N(CH_2)_2$**CN**), δ=127.9 ppm, d, J=160Hz (*m*-Ph), δ=129.2 ppm, d, J=160Hz (o-Ph), δ=134.3 ppm, m, (*i*-Ph), δ=151.9 ppm, m (C-Ph); δ=166.0 ppm, s (C=S)

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