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# SYNTHESIS OF SOME NEW HETEROCYCLIC **COMPOUNDS CONTAINING** THIENO[2,3-b]QUINOLINE MOIETY

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2-Cyano-3-amino-4-aryl-5, 6, 7, 8-tetrahydro-thieno[2,3-b]quinoline (1) reacted with carbon disulfide to give compound 2. Alkylation of 2 with different reagents gave the corresponding thioethers 3-7. Diazotisation of 1 furnished chloro derivative 8 which reacted with thiourea to give mercaptotriazine 9. Methylation of 9 yielded 10. On treatment of 8 with hydrazone hydrate, the expected hydrazinocompound 11 was obtained. Reaction of 11 with aromatic aldehydes, acetylacetone, acetic acid, acetic anhydride, carbon disulfide and nitrous acid gave compounds 12-17, respectively. The structures of all synthesized compounds were confirmed by elemental and spectral analysis.

Key words: Thienoquinolines; pyrimidine-dithiones; pyrimidine-dithioethers; chlorotriazines; mercaptotriazines; hydrazinotriazines and pyrazolyltriazines.

#### INTRODUCTION

It has been reported that some quinolines possess antimalarial and antifilarial and antihypertensive activity.<sup>1-4</sup> Also, the biological activity of many heterocyclic compounds containing thiophene ring has been reviewed.<sup>5,6</sup> On the other hand, the survey of the literature revealed that only few thieno[2,3-b]quinolines are known.<sup>7-10</sup> These observations prompted us to synthesize some new heterocyclic compounds containing a thieno[2,3-b]quinoline moiety.

#### RESULTS AND DISCUSSION

Reaction of 1<sub>a,b</sub> with carbon disulfide in pyridine gave 11-aryl-7,8,9,10-tetrahydroquinolino[3',2':4,5]thieno[3,2-d]pyrimidine-2,4(1H, 3H) dithiones (2<sub>a,b</sub>).<sup>11</sup>

<sup>\*</sup>Author to whom correspondence should be addressed.

Compound  $2_b$  underwent further reactions with different alkylating agents namely, alkyl (aralkyl) halides,  $\omega$ -bromoacetophenones, chloroacetanilides, chloroacetonitrile and ethyl chloroacetate to afford the corresponding 2,4-di(substituted thio)-11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]pyrimidines  $(3_{a-c})$ ,  $(4_{a-c})$ ,  $(5_{a-c})$ , (6) and (7) in good yields (Scheme 1).

Diazotisation of  $\mathbf{1}_{a,b}$  with sodium nitrite in concentrated hydrochloric acid led to the formation of 4-chloro-11-aryl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno-[3,2-d]-1,2,3-triazines ( $\mathbf{8}_{a,b}$ ). Compounds  $\mathbf{8}_{a,b}$  were reacted with thiourea to give the corresponding mercaptotriazine derivatives  $\mathbf{9}_{a,b}$ . Methylation of  $\mathbf{9}_{a,b}$  with methyl

iodide yielded 4-methylthio-11-aryl-7,8,9,10-tetrahydroquinolino[3',2':4,5]thieno-[3,2-d]-1,2,3-triazines ( $\mathbf{10_{a,b}}$ ). Condensation of  $\mathbf{8_{a,b}}$  with hydrazine hydrate furnished 4-hydrazino-11-aryl-7,8,9,10-tetrahydroquinolino[3',2':4,5]thieno[3,2-d]-1,2,3-triazines ( $\mathbf{11_{a,b}}$ ). Also, the latter compounds ( $\mathbf{11_{a,b}}$ ) were confirmed by another synthetic route through hydrazinolysis of methylthioderivatives  $\mathbf{10_{a,b}}$  (Scheme 2).

Condensation of 4-hydrazino-11-p-chlorophenyl-7,8,9,10-tetrohydro-quinolino-[3',2':4,5]thieno[3,2-d]-1,2,3-triazine  $(11_b)$  with aromatic aldehydes yielded the expected hydrazones  $12_{a,b}$ . Also, compound  $11_b$  was smoothly reacted with acetylacetone to give 4-(3,5-dimethylpyrazol-1-yl)-11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]-1,2,3-triazine (13) in excellent yield.

Reaction of  $11_b$  with acetic acid at refluxing temperature gave acetic acid, 2-(11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]-1,2,3-triazin-4-yl) hydrazide (14) while its interaction with acetic anhydride affording the triacetyl derivative 15.

Also, 11<sub>b</sub> was reacted with carbon disulfide in pyridine and/or with nitrous acid to furnish the promising pentacyclic compounds 16 and 17 respectively.

The structure of all synthesized compounds were elucidated on the basis of their elemental analysis (Table I) and spectroscopic data (Tables II, III).

$$\begin{array}{c} c_{6}H_{4}-c1(\underline{p}) \\ h_{1} \\ h_{2} \\ h_{3} \\ h_{4} \\ h_{5} \\ h_{6} \\ h$$

(17)

(16)

TABLE I
Physical and analytical data of all newly synthesized compounds (2-17)

No. (°C) % Formula C H N S CI C C C C C C C C C C C C C C C C C	Compound	Compound m.p. Yie	Yield	Molecular	 		% Calcd.		! ! ! ! !	 	 	% Found	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	No.	(၁.)	×	formula	၁	Ξ	z	S	C1	ပ	Ŧ	z	S	CI
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2a	338-40	7.1	C19H15N3S3	59.81		11.01	25.21	1	60.00	3.71	11.43	25.00	1
240 80 $C_{21}H_{18}C1N_{3}S_{3}$ 56.80 4.09 9.46 21.66 7.98 56.49 4.16 9.92 2 160-2 76 $C_{23}H_{22}C1N_{3}S_{3}$ 58.52 4.70 8.90 20.37 7.51 58.63 4.81 8.48 2 165-6 79 $C_{23}H_{22}C1N_{3}S_{3}$ 66.48 4.40 7.05 16.13 5.95 66.03 4.45 7.46 1 169-200 75 $C_{35}H_{26}C1N_{3}O_{2}S_{3}$ 66.49 4.40 7.05 16.13 5.95 66.03 4.45 7.46 1 198-200 75 $C_{35}H_{26}C1N_{3}O_{2}S_{3}$ 65.33 4.44 6.18 14.14 5.21 64.90 4.32 6.50 1 2.05-7 81 $C_{37}H_{36}C1N_{3}O_{2}S_{3}$ 51.90 2.99 5.19 11.87 - 51.51 2.85 5.34 1 1 2.05-7 78 $C_{35}H_{26}C1N_{3}O_{2}S_{3}$ 51.90 2.99 5.19 11.87 - 51.51 2.85 5.34 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	م	385-90		C19H14CIN3S3.	54.86	3.39	10.10	23.12	8.52	55.32	3.48	10.23	23.48	8.11
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	За	240	80	C,1H,8CIN3S3	56.80	4.09	9.46	21.66	7.98	56.49	4.16	9.92	21.46	8.35
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Ω	160-2	76	C23H22CIN3S3	58.52	4.70	8.90	20.37	7.51	58.63	4.81	8.48	20.11	7.20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	ပ	165-6	79	C33H26C1N3S3	66.48	04.4	7.05	16.13	5.95	66.03	4.45	7.46	16.50	6.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4.3	198-200	7.5	C35H2CIN30,S3	64.45	4.02	6.44	14.75	5.44	63.99	3.93		15.02	58.8
$ 220-3  78  C_{35}H_{24}\tilde{b}r_{2}C1N_{3}\tilde{o}_{2}S_{3}  51.90  2.99  5.19  11.87  -  51.51  2.85  5.34  1 $ $ 270-2  78  C_{35}H_{26}C1N_{5}\tilde{o}_{2}S_{3}  61.62  4.14  10.26  14.10  5.20  61.23  4.19  10.37  1 $ $ 250-2  73  C_{37}H_{32}C1N_{5}\tilde{o}_{4}S_{3}  59.87  4.34  9.43  12.96  4.78  60.00  4.25  9.30  1 $ $ 265-7  72  C_{35}H_{26}C1_{3}N_{5}\tilde{o}_{2}S_{3}  55.97  3.49  9.32  12.80  14.16  55.49  3.70  9.48  1 $ $ 178-80  86  C_{23}H_{16}C1N_{5}S_{3}  55.92  3.26  14.18  19.47  7.18  55.46  3.18  13.94  2 $ $ 125-6  85  C_{27}H_{26}C1N_{3}\tilde{o}_{4}S_{3}  55.14  4.46  7.14  16.35  6.03  54.87  4.66  6.71  1 $ $ 170-3  52  C_{18}H_{12}C1N_{4}S  61.27  3.71  15.88  9.09  10.05  61.50  3.90  15.78 $ $ 203-5  60  C_{18}H_{12}C1_{2}N_{4}S  55.82  3.12  14.47  8.28  18.31  55.39  3.18  14.33 $	۵	205-7	81	C37H30C1N3O2S3	65.33	47.4	6.18	14.14		64.90	4.32		14.06	5.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	ပ	220-3	78	C35H24Br2CIN3O2S3	51.90	2.99	5.19	11.87	ŧ	51.51	2.85	ĺ	12.09	ŀ
255-2 73 $C_{37}H_{32}CIN_{5}O_{4}S_{3}$ 59.87 4.34 9.43 12.96 4.78 60.00 4.25 9.30 1 265-7 72 $C_{35}H_{26}CI_{3}N_{5}O_{2}S_{3}$ 55.97 3.49 9.32 12.80 14.16 55.49 3.70 9.48 1 1 178-80 86 $C_{23}H_{16}CIN_{5}S_{3}$ 55.92 3.26 14.18 19.47 7.18 55.46 3.18 13.94 2 125-6 85 $C_{27}H_{26}CIN_{3}O_{4}S_{3}$ 55.14 4.46 7.14 16.35 6.03 54.87 4.66 6.71 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	5a	270-2	78	C35H2RCIN50,S3	61.62	4.14	10.26	14.10	5.20	61.23	4.19	10.37	14.55	5.60
265-7 72 $C_{35}H_{26}C_{13}H_{5}O_{2}S_{3}$ 55.97 3.49 9.32 12.80 14.16 55.49 3.70 9.48 1 178-80 86 $C_{23}H_{16}C_{11N}S_{3}$ 55.92 3.26 14.18 19.47 7.18 55.46 3.18 13.94 2 125-6 85 $C_{27}H_{26}C_{11N}S_{4}S_{3}$ 55.14 4.46 7.14 16.35 6.03 54.87 4.66 6.71 1 170-3 52 $C_{18}H_{12}C_{11N}S_{4}S_{3}$ 55.17 3.71 15.88 9.09 10.05 61.50 3.90 15.78 203-5 60 $C_{18}H_{12}C_{12}S_{4}S_{3}$ 55.82 3.12 14.47 8.28 18.31 55.39 3.18 14.33	۵	250-2	73	C37H32CIN5O453	59.87	4.34	9.43	12.96	4.78	00.09	4.25	9.30	12.50	4.43
178-80 86 $C_{23}H_{2}C_{11N_{5}S_{3}}$ 55.92 3.26 14.18 19.47 7.18 55.46 3.18 13.94 2 125-6 85 $C_{27}H_{2}C_{11N_{3}04_{4}S_{3}}$ 55.14 4.46 7.14 16.35 6.03 54.87 4.66 6.71 1 170-3 52 $C_{18}H_{12}C_{11N_{4}S}$ 61.27 3.71 15.88 9.09 10.05 61.50 3.90 15.78 203-5 60 $C_{18}H_{12}C_{12}N_{4}S$ 55.82 3.12 14.47 8.28 18.31 55.39 3.18 14.33	ڻ ب	265-7	72	C35H26C13N50253	55.97	3.49	9.32	12.80	14.16	55.49	3.70	9.48	13.22	14.55
125-6 85 $C_{27}H_{26}C_{11N_3}0_4S_3$ 55.14 4.46 7.14 16.35 6.03 54.87 4.66 6.71 1 1 170-3 52 $C_{18}H_{13}C_{11N_4}S$ 61.27 3.71 15.88 9.09 10.05 61.50 3.90 15.78 203-5 60 $C_{18}H_{12}C_{12}N_4S$ 55.82 3.12 14.47 8.28 18.31 55.39 3.18 14.33	9	178-80	98	C23H16C1N5S3	55.92	3.26	14.18	19.47	7.18	55.46	3.18	13.94	20.00	7.35
170-3 52 $C_{18}H_{13}C_{1N}_4$ S 61.27 3.71 15.88 9.09 10.05 61.50 3.90 15.78 203-5 60 $C_{18}H_{12}C_{12}N_4$ S 55.82 3.12 14.47 8.28 18.31 55.39 3.18 14.33	7	125-6	85	C27H26CIN304S3	55.14	94.4	7.14	16.35	6.03	54.87	4.66	6.71	16.00	6.31
203-5 60 $c_{18}^{H_{12}}c_{12}^{L_{14}}$ \$ 55.82 3.12 14.47 8.28 18.31 55.39 3.18 14.33	8a	170-3		C18H13CIN4S	61.27	3.71	15.88	60.6	10.05	61.50	3.90	15.78	9.47	9.47 10.50
	<b>a</b>	203-5		C18H12C12N4S	55.82	3.12	14.47	8.28	18.31	55.39	3.18	14.33	8.00	8.00 18.01

TABLE I (continud)

	Compound	Compound m.p. Yield	Yield	Molecular			% Calcd.			## ## ## ## ## ##	1)  )  )  )  )  )	* Found	() ()	() · () () () () () () () () () ()
b $215-7$ 91 $C_{18}H_{14}N_4S_2$ 61.69 4.03 15.99 18.30 $C_{18}H_{13}CIN_4S_2$ 56.17 3.40 14.56 16.66 16.254-6 82 $C_{19}H_{16}N_4S_2$ 62.61 4.42 15.37 17.59 $C_{19}H_{15}CIN_4S_2$ 62.61 4.42 15.37 17.59 $C_{19}H_{15}CIN_4S_2$ 62.05 4.63 24.12 9.20 $C_{24}H_{15}CIN_6S_2$ 62.05 4.63 24.12 9.20 $C_{25}H_{19}CIN_6S_2$ 62.03 4.63 24.12 9.20 $C_{25}H_{19}CIN_6S_2$ 62.33 4.22 16.77 6.40 $C_{26}H_{21}CIN_6S_2$ 62.33 4.22 16.77 6.40 $C_{26}H_{21}CIN_6S_2$ 61.81 4.28 18.80 7.17 152-4 80 $C_{24}H_{21}CIN_6S_2$ 56.54 4.03 19.78 7.55 $C_{24}H_{21}CIN_6S_2$ 56.54 4.16 16.51 6.30 $C_{24}H_{21}CIN_6S_2$ 53.71 3.08 19.78 15.09 $C_{24}H_{13}CIN_6S_2$ 53.71 3.08 19.78 8.14	No.	(0.)	<b>8</b> 9	formula	C	±	z	s	C1	ပ	I	z	s	CI
b $215-7$ 91 $C_{18}H_{13}CIN_4S_2$ 56.17 3.40 14.56 16.66  3a $254-6$ 82 $C_{19}H_{16}N_4S_2$ 62.61 4.42 15.37 17.59  b $235-7$ 83 $C_{19}H_{15}CIN_4S_2$ 62.65 4.63 24.12 9.20  b $246-7$ 94 $C_{18}H_{15}CIN_6S$ 62.05 4.63 24.12 9.20  c $244-5$ 96 $C_{25}H_{19}CIN_6S$ 62.33 4.22 16.77 6.40  c $225-6$ 90 $C_{23}H_{19}CIN_6S$ 62.33 4.22 16.77 6.40  d $225-6$ 90 $C_{23}H_{19}CIN_6S$ 61.81 4.28 18.80 7.17  l $45-7$ 76 $C_{20}H_{17}CIN_6S$ 56.54 4.03 19.78 7.55  152-4 80 $C_{24}H_{21}CIN_6S_2$ 56.64 4.16 16.51 6.30  280-3 72 $C_{19}H_{13}CIN_6S_2$ 53.71 3.08 19.78 15.09	9a	170-3	85	C18H14N4S2	61.69	4.03	15.99	18.30	ı	61.31		4.10 16.08	18.00	١.
3a $254-6$ 82 $C_{19}H_{16}N_{4}S_{2}$ 62.61 $4.42$ 15.37 17.59 b $235-7$ 83 $C_{19}H_{15}C1N_{4}S_{2}$ 57.21 3.79 $14.04$ 16.07 la $210-2$ 86 $C_{18}H_{16}N_{6}S$ 62.05 $4.63$ $24.12$ 9.20 b $246-7$ 94 $C_{18}H_{15}C1N_{6}S$ 62.05 $4.63$ $24.12$ 9.20 la $244-5$ 96 $C_{25}H_{19}C1N_{6}S$ 62.33 $4.22$ 16.77 6.40 b $242-3$ 95 $C_{26}H_{21}C1N_{6}S$ 62.33 $4.22$ 16.77 6.40 la $225-6$ 90 $C_{23}H_{19}C1N_{6}S$ 61.81 $4.28$ 18.80 7.17 145-7 76 $C_{20}H_{17}C1N_{6}S$ 56.54 $4.03$ 19.78 7.55 152-4 80 $C_{24}H_{21}C1N_{6}S_{2}$ 56.54 $4.03$ 19.78 15.09 $280-3$ 72 $C_{19}H_{13}C1N_{6}S_{2}$ 53.71 3.08 19.78 15.09 276-8 65 $C_{18}H_{12}C1N_{7}S$ 54.89 3.07 24.89 8.14	٩	215-7	91	C18H13C1N452	56.17	3.40	14.56	16.66	9.21	56.37	4.52	56.37 4.52 14.33	17.06	9.15
b $235-7$ 83 $C_{19}H_{15}CIN_{4}S_{2}$ 57.21 3.79 14.04 16.07 1a $210-2$ 86 $C_{18}H_{16}N_{6}S$ 62.05 4.63 24.12 9.20 b $244-5$ 94 $C_{16}H_{15}CIN_{6}S$ 63.76 4.07 17.84 6.81 b $244-5$ 95 $C_{26}H_{21}CIN_{6}S$ 62.33 4.22 16.77 6.40 1 $225-6$ 90 $C_{23}H_{19}CIN_{6}S$ 61.81 4.28 18.80 7.17 1 $145-7$ 76 $C_{20}H_{17}CIN_{6}OS$ 56.54 4.03 19.78 7.55 1 $152-4$ 80 $C_{24}H_{21}CIN_{6}O_{3}S$ 56.64 4.16 16.51 6.30 2 $280-3$ 72 $C_{19}H_{13}CIN_{6}S_{2}$ 53.71 3.08 19.78 15.09	10a	254-6	82	C19H16N4S2	62.61	4.42	15.37	17.59		63.06	4.50	63.06 4.50 15.07 18.08	18.08	1
la 210-2 86 C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> S 62.05 4.63 24.12 b 246-7 94 C <sub>18</sub> H <sub>15</sub> CIN <sub>6</sub> S 56.47 3.95 21.95 la 244-5 96 C <sub>25</sub> H <sub>19</sub> CIN <sub>6</sub> S 63.76 4.07 17.84 b 242-3 95 C <sub>26</sub> H <sub>21</sub> CIN <sub>6</sub> S 62.33 4.22 16.77 l 225-6 90 C <sub>23</sub> H <sub>19</sub> CIN <sub>6</sub> S 61.81 4.28 18.80 l 145-7 76 C <sub>20</sub> H <sub>17</sub> CIN <sub>6</sub> S 56.54 4.03 19.78 l 152-4 80 C <sub>24</sub> H <sub>21</sub> CIN <sub>6</sub> O <sub>3</sub> 56.64 4.16 16.51 280-3 72 C <sub>19</sub> H <sub>13</sub> CIN <sub>6</sub> S <sub>2</sub> 53.71 3.08 19.78 1	q	235-7	83	C19HISCIN4S2	57.21	3.79	14.04	16.07	8.89	57.22	3.90	57.22 3.90 14.26 16.45	16.45	8.68
b $246-7$ 94 $C_{18}H_{15}CIN_6S$ 56.47 3.95 21.95 24 $244-5$ 96 $C_{25}H_{19}CIN_6S$ 63.76 4.07 17.84 b $242-3$ 95 $C_{26}H_{21}CIN_6OS$ 62.33 4.22 16.77 225-6 90 $C_{23}H_{19}CIN_6S$ 61.81 4.28 18.80 145-7 76 $C_{20}H_{17}CIN_6OS$ 56.54 4.03 19.78 152-4 80 $C_{24}H_{21}CIN_6OS$ 56.64 4.16 16.51 280-3 72 $C_{19}H_{13}CIN_6S_2$ 53.71 3.08 19.78 1	11a	210-2	86	CIBHICNES	62.05	4.63	24.12	9.20		62.00	4.49	23.87	8.96	ŀ
ta 244-5 96 C <sub>25</sub> H <sub>19</sub> C1N <sub>6</sub> S 63.76 4.07 17.84 b 242-3 95 C <sub>26</sub> H <sub>21</sub> C1N <sub>6</sub> OS 62.33 4.22 16.77 i 225-6 90 C <sub>23</sub> H <sub>19</sub> C1N <sub>6</sub> S 61.81 4.28 18.80 l45-7 76 C <sub>20</sub> H <sub>17</sub> C1N <sub>6</sub> OS 56.54 4.03 19.78 l52-4 80 C <sub>24</sub> H <sub>21</sub> C1N <sub>6</sub> O <sub>3</sub> S 56.64 4.16 16.51 280-3 72 C <sub>19</sub> H <sub>13</sub> C1N <sub>6</sub> S <sub>2</sub> 53.71 3.08 19.78 1 276-8 65 C <sub>18</sub> H <sub>12</sub> C1N <sub>7</sub> S 54.89 3.07 24.89	p	246-7	94	C <sub>18</sub> H <sub>15</sub> CIN <sub>6</sub> S	56.47	3.95	21.95	8.37	9.26	56.03	4.16	56.03 4.16 22.12	8.52	9.21
b 242-3 95 C <sub>26</sub> H <sub>21</sub> CIN <sub>6</sub> 05 62.33 4.22 16.77 225-6 90 C <sub>23</sub> H <sub>19</sub> CIN <sub>6</sub> S 61.81 4.28 18.80 145-7 76 C <sub>20</sub> H <sub>17</sub> CIN <sub>6</sub> 0S 56.54 4.03 19.78 152-4 80 C <sub>24</sub> H <sub>21</sub> CIN <sub>6</sub> 0 <sub>3</sub> S 56.64 4.16 16.51 280-3 72 C <sub>19</sub> H <sub>13</sub> CIN <sub>6</sub> S <sub>2</sub> 53.71 3.08 19.78 1 276-8 65 C <sub>18</sub> H <sub>12</sub> CIN <sub>7</sub> S 54.89 3.07 24.89	12a	244-5	96	C,5H19CINES	63.76	4.07	17.84	6.81	7.53	63.35	63.35 3.92 17.41	17.41	6.50	6.50 8.00
145-7 76 C <sub>20</sub> H <sub>17</sub> CIN <sub>6</sub> S 61.81 4.28 18.80 152-4 80 C <sub>24</sub> H <sub>21</sub> CIN <sub>6</sub> 0 <sub>3</sub> S 56.54 4.03 19.78 280-3 72 C <sub>19</sub> H <sub>13</sub> CIN <sub>6</sub> S <sub>2</sub> 53.71 3.08 19.78 1 276-8 65 C <sub>18</sub> H <sub>12</sub> CIN <sub>7</sub> S 54.89 3.07 24.89	۵	242-3	95	C26H21CIN60S	62.33	4.22	16.77	6.40	7.08	62.09	62.09 4.25 17.08	17.08	6.59	7.21
145-7 76 C <sub>20</sub> H <sub>17</sub> CIN <sub>6</sub> 0S 56.54 4.03 19.78 152-4 80 C <sub>24</sub> H <sub>21</sub> CIN <sub>6</sub> 0 <sub>3</sub> S 56.64 4.16 16.51 280-3 72 C <sub>19</sub> H <sub>13</sub> CIN <sub>6</sub> S <sub>2</sub> 53.71 3.08 19.78 1 276-8 65 C <sub>18</sub> H <sub>1</sub> ,CIN <sub>7</sub> S 54.89 3.07 24.89	13	225-6	90	C23H19CIN6S	61.81	4.28	18.80	7.17	7.93	62.03	4.40	62.03 4.40 19.25	7.00	7.00 7.66
152-4 80 C <sub>24</sub> H <sub>21</sub> CIN <sub>6</sub> 0 <sub>3</sub> S 280-3 72 C <sub>19</sub> H <sub>13</sub> CIN <sub>6</sub> S <sub>2</sub> 276-8 65 C <sub>18</sub> H <sub>1</sub> ,CIN <sub>7</sub> S	14	145-7	92	C20H17CIN60S	56.54	4.03	19.78	7.55	8.34	56.10	56.10 4.12 19.93	19.93	7.13	8.08
280-3 72 C <sub>19</sub> H <sub>13</sub> CIN <sub>6</sub> S <sub>2</sub> 276-8 65 C <sub>1R</sub> H, CIN <sub>7</sub> S	15	152-4	80	C24H21C1N603S	56.64	4.16	16.51	6.30	6.97	56.45 4.00 16.31	4.00	16.31	6.78	7.11
276-8 65 C <sub>1 R</sub> H <sub>1</sub> ,ClN <sub>7</sub> S 54.89 3.07 24.89	91	280-3	72	C19H13C1N6S2	53.71	3.08	19.78	15.09	8.34	53.98	3.00	53.98 3.00 20.09 15.37	15.37	8.06
7 7 01	71	276-8	65	C18H12C1N7S	54.89	3.07	24.89	8.14	9.00	54.75	2.88	54.75 2.88 24.79	8.20 9.41	9.41

TABLE II
Important IR bands of the synthesized compounds (2-17)

==========	=======================================	===========		========
Assignment	νC=0	NH	vC=N	vCH ali.
2 <sub>a,b</sub> *	<u>-</u>	3360-3350	1570	2940
3 <sub>a-c</sub>	-	-	1600	2940,2860
4 a - c	1690-1680	-	1600	2940
5 a-c	1660-1655	3290-3270	1600	2940
6**	-	-	1600	2940
7	1740	-	1600	2980,2940
<sup>8</sup> a,b	-	-	1590	2940
<sup>9</sup> a,b	-	3100	1590	2940
<sup>10</sup> a,b	<b>-</b>	-	1600	2940
ll <sub>a,b</sub>	-	3300,3200	1650,1600	2940,2860
12 <sub>a,b</sub>	-	3200-3180	1610,1590	2940,2840
13	-	-	1590	2940,2860
14	1670	3480,3250	1600	2940,2860
15	1730,1690	-	1590,1570	2940,2860
16	-	3380	1590	2940
17	-	-	1600	2940
=======================================		=======================================	========	=========

 $<sup>^*</sup>$ A band at 1220 cm $^{-1}$  for  $\nu$ C=S.

<sup>\*\*</sup>A band at 2250 cm $^{-1}$  for  $\nu$ C $\Xi$ N.

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<sup>1</sup>H-NMR spectra of representative examples of the synthesized compounds (chemical shifts in δppm) TABLE III

Compound		-CH <sub>2</sub> -at C-7.	-CH <sub>2</sub> -at C-10	$-(CH_2)_2$ -at C-8,9	200440
O	protons	(t)	(t)	(E)	erpubre Janno
2a (CF <sub>3</sub> CO <sub>2</sub> H)	7.20-7.80(m,5H)	3.20-3.45	2.50-2.75	1.70-2.20	
3a (CDC1 <sub>3</sub> )	7.00-7.50(9,4H)	3.00-3.25	2.30-2.55	1.50-1.90	2.65(s, 3H, SCH <sub>3</sub> at C-2). 1.80(s, 3H, SCH <sub>3</sub> at C-4).
4a (CDC1 <sub>3</sub> )	6.90-8.00(m,14H)	3.00-3.25	2.30-2.55	1.50-2.00	4.75(s,2H,5CH <sub>2</sub> CO at C-2). 3.80(s,2H,5CH <sub>2</sub> CO at C-4).
5b (CDC1 <sub>3</sub> )	6.60-7.55(m,12H)	3.05-3.30	2.35-2.60	1.60-2.10	4.00(s,2H,SCH <sub>2</sub> CON at C-2). 3.50(s,2H,SCH <sub>2</sub> CON at C-4). 3.70(s, 6H, two OCH <sub>3</sub> ).
7 (CDCL <sub>3</sub> )	7.00-7.50(q,4H)	3.05-3.30	2.35-2.60	1.60-2.10	4.05(s,2H,5CH <sub>2</sub> COO at C-2). 3.40(s,2H,5CH <sub>2</sub> COO at C-4). 4.10-4.40(q,4H, two COOCH <sub>2</sub> ). 1.20-1.45(t,6H, two CH <sub>3</sub> ).
8a (CDC1 <sub>3</sub> )	7.10-7.60(m,5H)	3.05-3.30	2.50-2.75	1.60-2.10	
10b (CDC1 <sub>3</sub> )	7.15-1.60(q,4H)	3.05-3.30	2.50-2.75	1.65-2.15	2.85(s,3H,SCH <sub>3</sub> ).

TABLE III (continued)

Compound No.	Aromatic protons	-CH <sub>2</sub> -at C-7 (t)	-CH <sub>2</sub> -at C-10 (t)	-(CH <sub>2</sub> ) <sub>2</sub> -at C-8,9 (m)	Other signals
11b (DMSO)	7.20-7.60(q,4H)	3.00-3.20		1.40-1.90	5.00(s,2H,NH <sub>2</sub> ) 9.50(s,1H,NH).
13 (CDC1 <sub>3</sub> )	7.15-7.60(9,4H)	3.05-3.30	2.50-2.75	1.60-2.10	2.30(s,3H,CH <sub>3</sub> ) 2.80(s,3H,CH <sub>3</sub> ) 6.10(s,1H,CH).
14 (CDC1 <sub>3</sub> )	7.10-7.60(m,4H)	3.00-3.25			1.50-2.60[m,9H,CH <sub>3</sub> ,CH <sub>2</sub> and (CH <sub>2</sub> ) <sub>2</sub> ]
15 (CDC1 <sub>3</sub> )	7.00-7.50(m,4H)	3.05-3.30			1.50-2.50[m,15H;3CH <sub>3</sub> , CH <sub>2</sub> and (CH <sub>2</sub> ) <sub>2</sub> ]
16 (CF <sub>3</sub> CO <sub>2</sub> H)	7.25-7.65(9,4H)	(3.20-3.40)*	(2.40-2.60)**	(1.65-2.10)	
17 (CF <sub>3</sub> CO <sub>2</sub> H)	7.20-7.60(9,4H)	(3.20-3.40)*	(2.55-2.80)**	(1.60-2.15)***	

\*\* -CH<sub>2</sub>-at C-8 \*\*\* -(CH<sub>2</sub>)<sub>2</sub>-at C-9,10

#### EXPERIMENTAL

All melting points were determined on a kofler melting point apparatus and are uncorrected. IR spectra were obtained using a Pye-Unicam SP3-100 infrared spectrophotometer. NMR spectra were recorded by a Varian EM-390 MHZ spectrometer using TMS as internal standard.

The physical and analytical data of all newly synthesized compounds are depicted in Table I.

2-Cyano-3-amino-4-aryl-5,6,7,8-tetrahydro-thieno[2,3-b]quinolines ( $\mathbf{1}_{a,b}$ ). These compounds were prepared according to the literature method.<sup>10</sup>

11-Aryl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]-pyrimidin-2,4-(1H,3H) dithiones  $(2_{a,b})$ . A mixture of  $1_{a,b}$  (0.01 mol) and carbon disulfide (5 ml) in dry pyridine was heated on a water bath for 6 hrs. The solvent was removed by distillation under reduced pressure and the residue was crystallized from pyridine to give  $2_{a,b}$  as orange plates.

Alkylation of compound 2h.

General procedure.

A mixture of  $2_b$  (0.01 mol), alkylating agent (0.022 mol) and anhydrous sodium acetate (2 g) in ethanol (60 ml) was refluxed for 1 hr. The resultant product was crystallized from ethanol.

The following compounds (3-7) were prepared as in the above general procedure.

- a) 2,4-Di(alkyl/aralkyl) thio-11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]-pyrimidines (3<sub>a-c</sub>). These compounds were prepared by using the corresponding alkyl (aralkyl) halides.
- b) 2,4-Di(aroylmethylthio)-11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino [3',2':4,5] thieno [3,2-d]pyrimidines  $(\mathbf{4}_{n-k})$ . These compounds were prepared by using phenacyl bromide and its derivatives.
- c) 2,4-Di(N-arylcarboxamidomethylthio)-11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]pyrimidines ( $\mathbf{5}_{n-c}$ ). These compounds were prepared by using N-chloroacetylated aromatic amines.
- d) 2,4-Di(cyanomethylthio)-11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]pyrimidine (6). This compound was prepared by using chloroacetonitrile.
- e) 2,4-Di(ethoxycarbonylmethylthio)-11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno-[3,2-d]pyrimidine (7). This compound was prepared by using ethyl chloroacetate.
- 4-Chloro-11-aryl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]-1,2,3-triazines ( $\mathbf{8_{a,b}}$ ). To a cold solution of  $\mathbf{1_{a,b}}$  (0.011 mol) in 30 ml of acetic acid and 15 ml of concentrated hydrochloric acid, was added a solution of 0.95 g (0.014 mol) of sodium nitrite in 10 ml of water. After completion of addition, the ice bath was removed and stirring continued for 2 more hours. The crude product was crystallized from ethanol to give  $\mathbf{8_{a,b}}$  in the form of faint pink needles.
- 4-Mercapto-11-aryl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]-1,2,3-triazines  $(9_{a,b})$ . A mixture of  $8_{a,b}$  (0.01 mol) and thiorea (0.012 mol) in dry methanol (40 ml) was heated under reflux for 3 hrs. The separated yellow crystalline solid was collected, washed with ethanol and heated with 10% aqueous sodium hydroxide (15 ml) at 50°C for 15 min. On cooling and acidification with acetic acid, compounds  $9_{a,b}$  were obtained as yellow powders and were crystallized from ethanol-chloroform as yellow needles.
- 4-Methylthio-11-aryl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]-1,2,3-triazines ( $\mathbf{10}_{a,b}$ ). To a solution of 0.02 mole of  $\mathbf{9}_{a,b}$  in 40 ml of 5% sodium hydroxide was added 5 ml of methyl iodide, and the mixture was stirred for 2 hrs. The solid thus formed was collected and crystallized from ethanol in the form of colourless plates.
- 4-Hydrazino-11-aryl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]-1,2,3-triazines ( $11_{a,b}$ ).

#### Method A.

A mixture of  $\mathbf{8}_{a,b}$  (0.01 mol) and hydrazine hydrate (3 ml) in ethanol (40 ml) was refluxed for 1 hr. The white solid thus obtained was crystallized from ethanol-chloroform mixture.

#### Method B.

To a suspension of  $10_{a,b}$  (0.01 mol) in ethanol (30 ml), 3 ml hydrazine hydrate was added. The reaction mixture was refluxed on a water bath for 3 hrs. Cooling yielded white products which upon recrystallization were identical to those described in method A.

Aromatic aldehydes, (11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]-1,2,3-tria-zin-4-yl) hydrazones (12<sub>a,b</sub>). A mixture of 11<sub>b</sub> (0.01 mol) and the required aromatic aldehyde (0.01 mol) was refluxed in ethanol for 3 hrs. The solid product was filtered off and recrystallized from dioxane to give 12<sub>a,b</sub> in the form of yellowish white needles.

4-(3,5-Dimethylpyrazol-1-yl)-11-p-chlorophenyl-7,8,9,10-tetrahydro-equinolino[3',2':4,5]thieno[3,2-d]-1,2,3-triazine (13). Compound 11<sub>b</sub> (0.002 mol) and acetylacetone (2 ml) were refluxed in ethanol (30 ml) for 3 hrs. The product was collected and recrystallized from ethanol as pale yellow needles.

Acetic acid, 2-(11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino[3',2':4,5]thieno[3,2-d]-1,2,3-triazin-4-yl) hydrazide (14). Compound 11<sub>b</sub> (0.5 g) and acetic acid (20 ml) were refluxed for 5 hrs. The cooled reaction mixture was diluted with water and the precipitate was collected and recrystallized from benzene-pet. ether to give pale yellow needles.

1,2,2-Triacetyl-1-(11-p-chlorophenyl-7,8,9,10-tetrahydro-quinolino [3',2':4,5] thieno [3,2-d]-1,2,3-triazin-4-yl) hydrazine (15). A mixture of compound  $11_b(0.5 \text{ g})$  and acetic anhydride (30 ml) was refluxed for 5 hrs. The reaction mixture was cooled and diluted with water, the solid thus obtained was filtered off and crystallized from benzene-pet. ether (40-60) as white needles.

7-P-chlorophenyl-8,9,10,11-tetrahydro-quinolino [3',2':4,5] thieno [2,3-e]-s-triazolo[4,3-c]-1,2,3-triazin-4 (3H) thione (16). A mixture of compound 11<sub>b</sub> (0.5 g) and carbon disulfide (2 ml) in dry pyridine (10 ml) was heated on a water bath for 5 hrs. The reaction mixture was concentrated, diluted with water and neutralized with acetic acid whereby a yellow solid precipitated. It was crystallized from ethanol as yellow needles.

7-P-chlorophenyl-8,9,10,11-tetrahydro-quinolino[3',2':4,5]thieno[2,3-c]tetrazolo[1,5-c]-1,2,3-triazine (17). Sodium nitrite solution (7 ml, 10%, 0.01 mol) was added dropwise to a solution of compound  $11_b$  (0.002 mol) in concentrated hydrochloric acid (5 ml) at 0°C with stirring. The solid product was crystallized from ethanol as white needles.

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