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NOTE

FLOW-VACUUM PYROLYSIS OF POLYCYCLIC COMPOUNDS. 25[1]. PYROLYSIS OF SOME 3-MERCAPTO-5-SUBSTITUTED-1,2,4-TRIAZOLES

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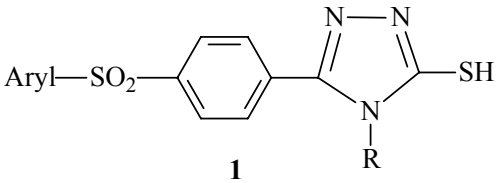
The flow-vacuum pyrolysis (FVP) of the 3-mercapto-5-substituted-1,2,4-triazoles **5a-c**, between 475^{0}C – 750^{0}C, at 2 mm Hg, in inert atmosphere (4mL/min argon flow rate) and quartz pyrolysis tube (60 cm length, 1 cm internal diameter, quartz chips filling 30 mm long) afforded a complex mixture with cyano-diphenyl-sulphones **12a-c** and corresponding diphenylsulphones **13a-c** as main products. The reaction products were identified by GC/ MS. A radical mechanism is suggested in order to explain the formation of the main reaction products.

INTRODUCTION

Flow and/or flash-vacuum pyrolysis is a useful technique to study reaction mechanisms and for synthetic purposes[2] as well. This method enables the isolation of kinetically controlled products and/or avoidance subsequent reactions.

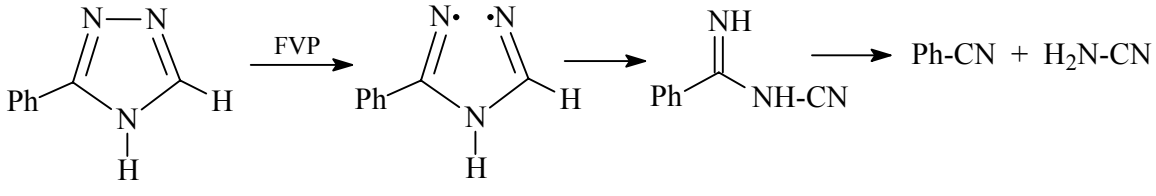
Substituted triazoles **1**, especially mercaptotriazoles, were utilized as physiologically active compounds[3] (with antiparasitic,[4a] anticonvulsivant,[4b] antimicrobial and antiviral activity,[4c,d] as well as izozyme II of carbonic anhydrase inhibitors[4e]).



1

R: H, Alkyl

The first study of vacuum pyrolysis of substituted 1,2,4-triazoles was performed by Gilchrist[5] at 600-800^{0}C (Scheme 1):



2 **3** **4**

Scheme 1

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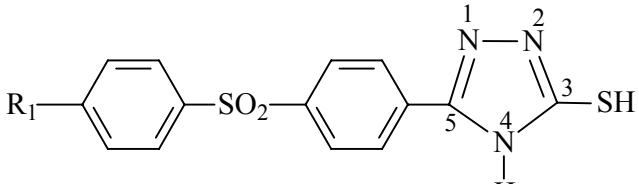
The Gilchrist's proposed mechanism for the flash vacuum pyrolysis of 1,2,4-triazoles involves, on a route, rearrangement followed by N_2 extrusion and, on the other route, the cleavage of N-N bond, followed by extrusion of a nitrile fragment. Phenyl substitution of triazole ring would favor the second route.[5b]

In this paper we describe the thermal behavior of four related 4,5-disubstituted-3-mercapto-1,2,4-triazoles **5a-c** in flow-vacuum pyrolysis between 475-750°C.



5a : R_1 = H
5b : R_1 = Cl
5c : R_1 = Br

RESULTS AND DISCUSSION

Syntheses

The substituted triazoles **5** were obtained in a five-step synthesis using literature data[6] by the cyclisation of corresponding 1-aroyl-thiosemicarbazides **6** in alkaline solution (Scheme 2).

Pyrolyses

General procedure

The flow-vacuum pyrolyses of **5** were performed in our previously described apparatus[7] with a pyrolysis quartz tube (60 cm length, 10 mm internal diameter) filled with quartz chips on 30 cm length; this zone was heated in a vertical cylindrical electric oven. The temperature was continuously measured by a thermocouple and the pressure (~2 mmHg) with a McLeod manometer. The sample (usually ~ 30 mg) was sublimed under argon flow (4 ml/min) in the pyrolysis tube.

The reaction products were dissolved in dichloromethane, the solvent was evaporated *in vacuo* and the residue was analysed by GC/MS*. Analytical pyrolyses at optimal temperature were followed by preparative runs in order to isolate the main products or for IR** spectra registration.

The main products of flow-vacuum pyrolyses of 4,5-disubstituted-3-mercapto-1,2,4-triazoles **5a-c** are presented in Scheme 3.

The product distribution versus temperature are presented in Tables 1 – 3 and spectral data for the main products are given below.

Mass spectrum of **12a** (m/e; relative abundance, %): 27 (1.7); 38 (1.1); 39 (4.8); 50 (13.8); 51 (38.3); 52 (3.4); 53 (1.8); 62 (1.4); 63 (2.7); 65 (15.5); 69 (1.5); 74 (5.6); 75 (12.9); 76 (11.2); 77 (60); 78 (5.5; 89 (2.9); 93 (14.8); 97 (12.7); 102 (15.4); 122 (6); 125 (100; B.P.); 126 (8); 127 (5.4); 149 (4.9); 150 (44); 151 (7.9); 152 (3.9); 177 (3.5); 178 (4.1); 179 (2,5); 195 (1,7); 243 (M; 75,6); 244 (M + 1; 12); 245 (4,2).

IR spectrum of **12a** ($CHCl_3$, ν, cm^{-1}): 843w; 1016w; 1107m; 1160i; 1324m; 1461m; 2363vw; 2963s; 3447w.

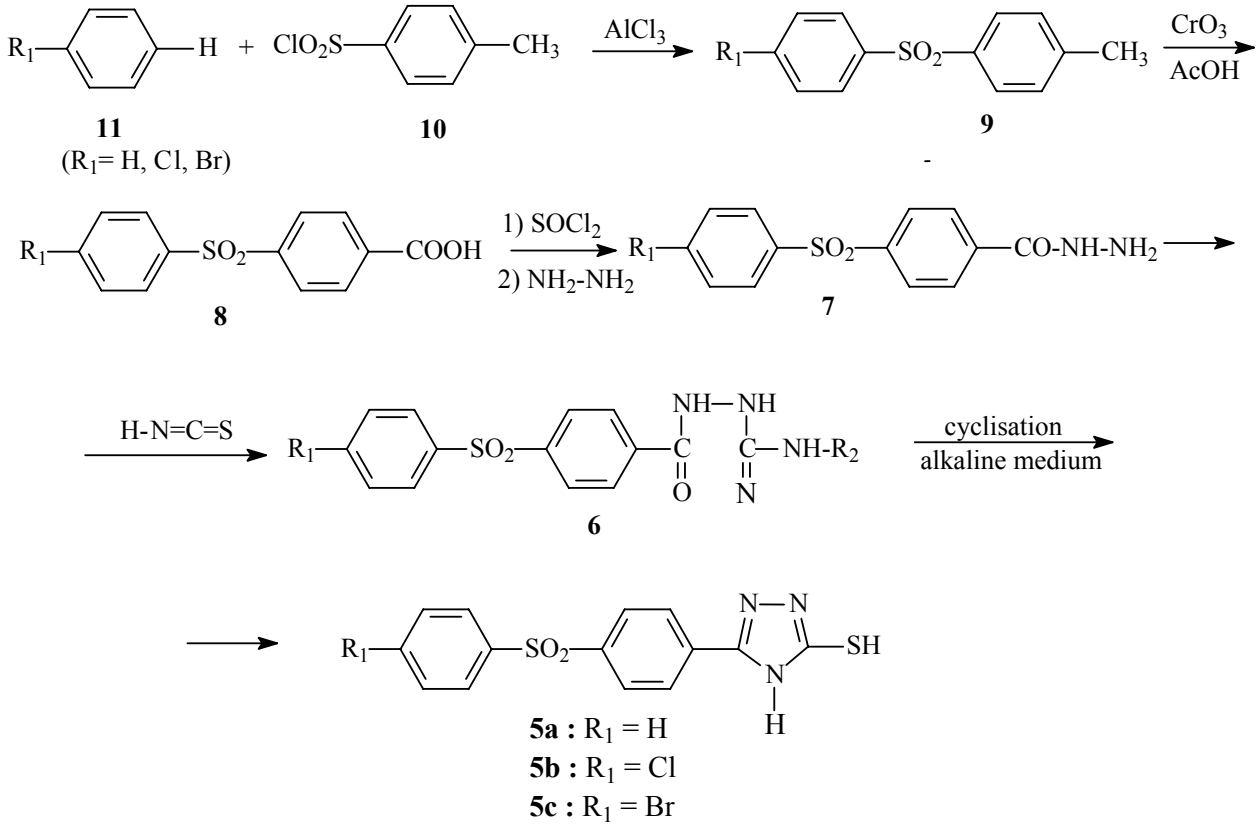
Mass spectrum of **13a** (m/e; relative abundance, %): 27 (1.2); 39 (3,2); 50 (9,2); 51 (27,9); 52 (2,2); 53 (2,1); 65 (4,9); 74 (3,4); 75 (2,7); 76 (4,2); 77 (43,3); 78 (4,3); 81 (1,8); 97 (18,6); 98 (1,3); 109 (1,6); 125 (BP; 100); 126 (8,9); 127 (5,5); 151 (1,9); 152 (8,2); 154 (1,8); 217 (2,1); 218 (M; 45); 219 (M+1; 7,1).

Mass spectrum of **15** (m/e; relative abundance, %): 37 (1.8); 38 (2.1); 39 (6) 45 (4.8); 50 (5.2); 51 (10.6); 54 (1.4); 55 (2.9); 57 (3); 58 (2.1); 59 (1); 61 (1.8); 62 (1.2); 63 (4.9); 64 (1.1); 65 (9.3); 66 (25.1); 67 (2.5); 68 (1); 69 (9.5); 70 (1.3); 71 (2.5); 74 (2.3); 77 (11.7); 78 (2.8) 81 (2.9); 82 (4.7); 84 (19.8) 95 (2.3); 108 (40); 109 (24.5); 110 (B.P.; M; 100); 111 (M + 1; 9.4); 112 (M + 2; 6).

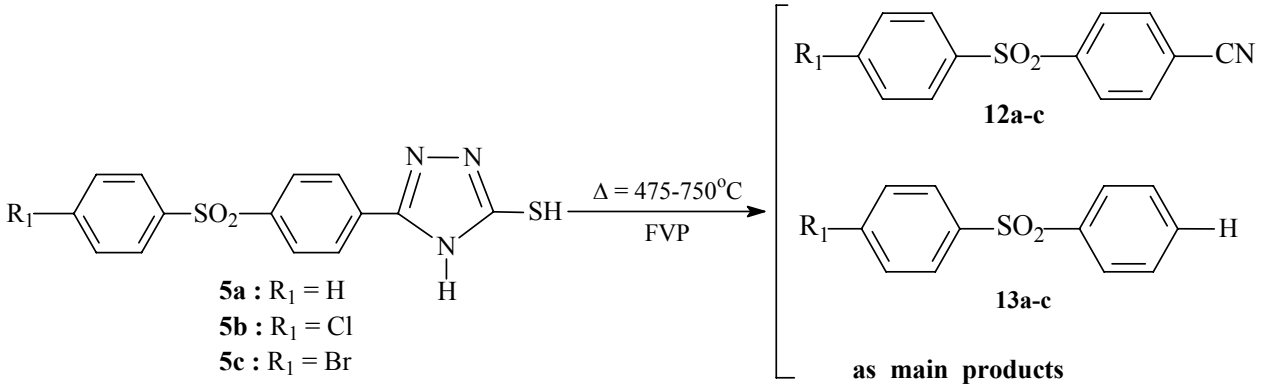
Mass spectrum of **17** (m/e; relative abundance, %): 39 (3.1); 44 (5.3); 50 (11); 51 (21.5); 52 (2.2); 53 (1.7); 65 (7.2); 74 (4.8); 75 (8.1); 76 (13.5); 77 (38.8); 78 (3.7); 81 (1.4); 92 (2.1); 97 (12); 104 (92); 105 (1.1); 108 (3); 109 (2.8); 121 (1.2); 125 (B.P.; 100) 126 (8.4); 127 (5.4); 128 (1.5); 140 (4.9); 141 (5.5); 152 (15.7); 153 (4.4); 168 (39.8); 169 (3.9); 170 (2.1); 181 (1.7); 245 (64.5); 246 (9.4); 247 (3.7); 261 (M; 93.3); 262 (M + 1; 15.3); 263 (M+2; 5.3).

* Agilent GC/MS with split/splitless injector, quadrupole, a capillary DB-5-MS (25 m length, 0.25 mm internal diameter, carrier gas: helium (flow-rate of 0.5 mL/min); temperature program: 50°C – 100°C at 5°C/min, 100°C – 280°C at 10°C/min and then 15 min. at 280°C; electron ionisation: 70.

** IR spectra were registered on a Bruker Equinox spectrometer.



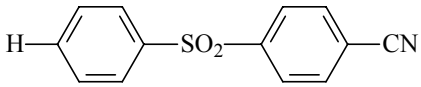
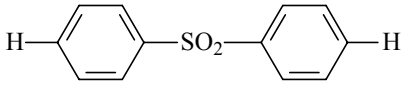
Scheme 2



Scheme 3

Table 1

Pyrolyses products distribution of (phenylsulphonyl)phenyl-3-mercapto-1,2,4-triazole (**5a**)

Product	Chemical structure	475°C (%)	550°C (%)	750°C (%)
12a	 **M = 243**	67.1	79	83.9
13a	 **M = 218**	6.4	7.5	9.1

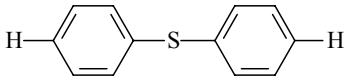
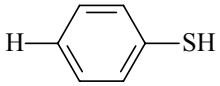
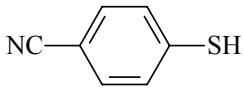
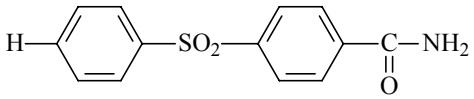
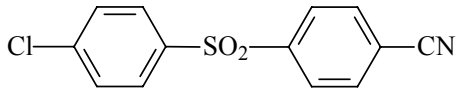
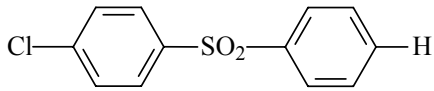
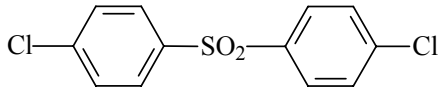
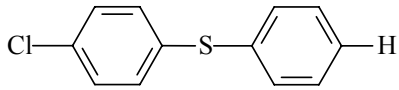
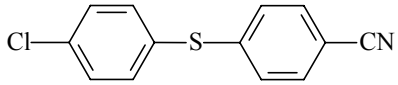
14	 **M = 186**	0.4	0.2	0.1
15	 **M = 110**	5.9	5	0.8
16	 **M = 135**	0.6	0.8	1.1
17	 **M = 261**	5.7	1	0.8

Table 2

Pyrolyses products distribution of 5-*p*-(*p*-chlorophenylsulphonyl)phenyl-3-mercapto-1,2,4-triazole (**5b**)

Product	**Chemical structure**	**475°C (%)**	**550°C (%)**	**750°C (%)**
12b	 **M = 277**	60.6	56	40.2
13b	 **M = 252**	12.1	10.4	16
18	 **M = 286**	3.9	3.8	4
19	 **M = 220**	6	-	-
20	 **M = 245**	-	-	5

Mass spectrum of **12b** (m/e; relative abundance, %): 49 (6); 50 (49); 51 (37); 52 (6); 55 (9); 57 (8); 63 (13); 68 (8); 70 (12); 73 (21); 74 (29); 75 (100; B.P.); 76 (30); 81 (8); 83 (8); 85 (10); 87 (8); 95 (11); 97 (8); 99 (34); 100 (7); 101 (12); 102 (32); 111 (63); 112 (6); 113 (19); 122 (15); 127 (72); 129 (21); 133 (10); 150 (37); 151 (8); 159 (85); 160 (9); 174 (11); 177 (14); 207 (16); 208 (6); 242 (15); 253 (5); 276 (61); 277 (17; M.P.); 278 (23; M+1); 279 (6; M+2).

IR spectrum of **12b** ($CHCl_3$, ν, cm^{-1}): 1090w, 1160w, 1218i, 1364w, 1711m, 2360m, 3019w.

Mass spectrum of **13b** (m/e; relative abundance, %): 50 (29); 51 (48); 63 (5); 74 (12); 75 (31); 77 (40); 97 (46); 99 (5); 111 (19); 113 (7); 125 (100; B.P.); 126 (9); 127 (7); 131 (10); 133 (5); 153 (10); 159 (41); 161 (14); 251 (31); 252 (107; M.P.); 253 (12; M+1).

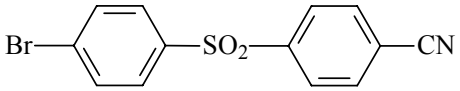
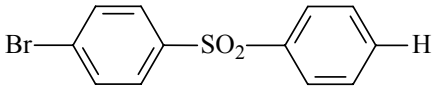
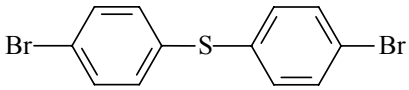
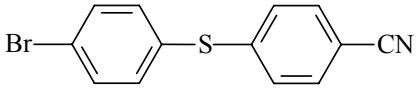
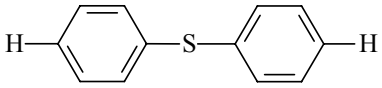
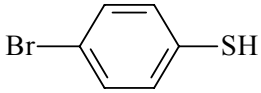
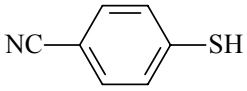
Mass spectrum of **12c** (m/e; relative abundance, %): 37 (2); 38 (3.2); 39 (2.2); 40 (2.9); 50 (36); 51 (14.5); 52 (2.6); 62 (2.9); 63 (12.2); 64 (6.2); 70 (2.1); 74 (22.4); 75 (58.3); 76 (56.3); 77 (5.5); 79 (2.3); 89 (7.4); 92 (2.3); 96 (7.9); 100 (2.2); 102 (30.3); 103 (5.1); 119 (3.2); 122 (8); 124 (3.6); 125 (5.9); 128 (4.6); 129 (4.4); 134 (2.6); 143 (21.2);

145 (16.2); 150 (38.9); 151 (9.6); 152 (3.6); 155 (37.6); 157 (39); 158 (3.2); 166 (4); 171 (64); 173 (59.4), 175 (6.7); 177 (16.2); 203 (68.5); 204 (5.9); 205 (74.8); 206 (5.4); 219 (6.4); 221 (6.7); 242 (12.9); 321 (M; 87.9); 323 (M+2; 100); 324 (20.8); 325 (6.9).

IR spectrum of **12c** ($CHCl_3$, ν, cm^{-1}): 1090w, 1160w, 1218i, 1364w, 1711m, 2360m, 3019w.

Table 3

Pyrolyses products distribution of 5-*p*-(*p*-bromophenylsulphonyl)phenyl-3-mercapto-1,2,4-triazole (**5c**)

Product	Chemical structure	475°C (%)	650°C (%)	750°C (%)
12c	 **M = 321**	50	60	34.7
13c	 **M = 296**	11.3	25.7	62.3
21	 **M = 342**	15.6	1	0.14
22	 **M = 289**	3.6	0.7	0.1
23	 **M = 186**	1.3	9.8	1.4
24	 **M = 190**	5.9	0.4	0.6
25	 **M = 135**	2.2	2.3	0.7

Mass spectrum of **13c** (m/e; relative abundance, %): 39 (2.1); 50 (17); 51 (23.1); 63 (3.1); 65 (2.6); 74 (8.6); 75 (15.9); 76 (18); 77 (33.8); 78 (2.7); 96 (4.1); 97 (12.6); 125 (B.P.; 100); 126 (9.2); 127 (5.9); 143 (2.6); 151 (3.5); 152 (12.6); 155 (9.1); 157 (9); 171 (2.9); 177 (2.4); 203 (29.6); 204 (2.4); 205 (29.5); 206 (2.4); 296 (M; 43); 297 (M+1; 7.4); 298 (M+2; 45).

Mass spectrum of **21**(m/e; relative abundance, %): 27 (2.3); 50 (4.6); 63 (4.2); 69 (6.4); 74 (3.4); 75 (6.2); 76 (6.4); 81 (3.1); 82 (4.1); 92 (13.1); 108 (26.9); 139 (9.4); 140 (3.4); 152 (5.4); 182 (2.4); 263 (22.3); 264 (9.2); 265 (22.5); 266 (6.1); 342 (M; 49.3); 344 (B.P.; M+2; 100); 345 (13.3); 346 (47.8); 348 (2.4).

Mass spectrum of **23** (m/e; relative abundance, %): 18 (19.6); 29 (4.2); 32 (14.3); 41 (3.9); 52 (2.9); 63 (5.6); 65 (5.4); 69 (5.3); 80 (3); 83 (2.6); 85 (27); 89 (32); 94 (4.5); 96 (2.6); 108 (4.8); 109 (7.5); 142 (3.7); 151 (3.8); 152 (5.4); 183 (3); 185 (B.P.; 100); 186 (M; 93.3); 187 (5.2).

Mass spectrum of **24** (m/e; relative abundance, %): 26 (4); 31 (2); 37 (5.4); 39 (7.9); 50 (8.3); 54 (3.3); 57 (4.4); 61 (3.6); 62 (3.7); 63 (10); 65 (18.3); 74 (6.4); 75 (7.9); 76 (6.7); 108 (15.4); 109 (B.P. 100); 110 (7.9); 111 (4.4); 139 (3.3); 155 (4.1); 181 (2.3); 187 (3.8); 188 (59.7); 189 (6.6); 190 (M; 57.9); 191 (M+1; 6.4).

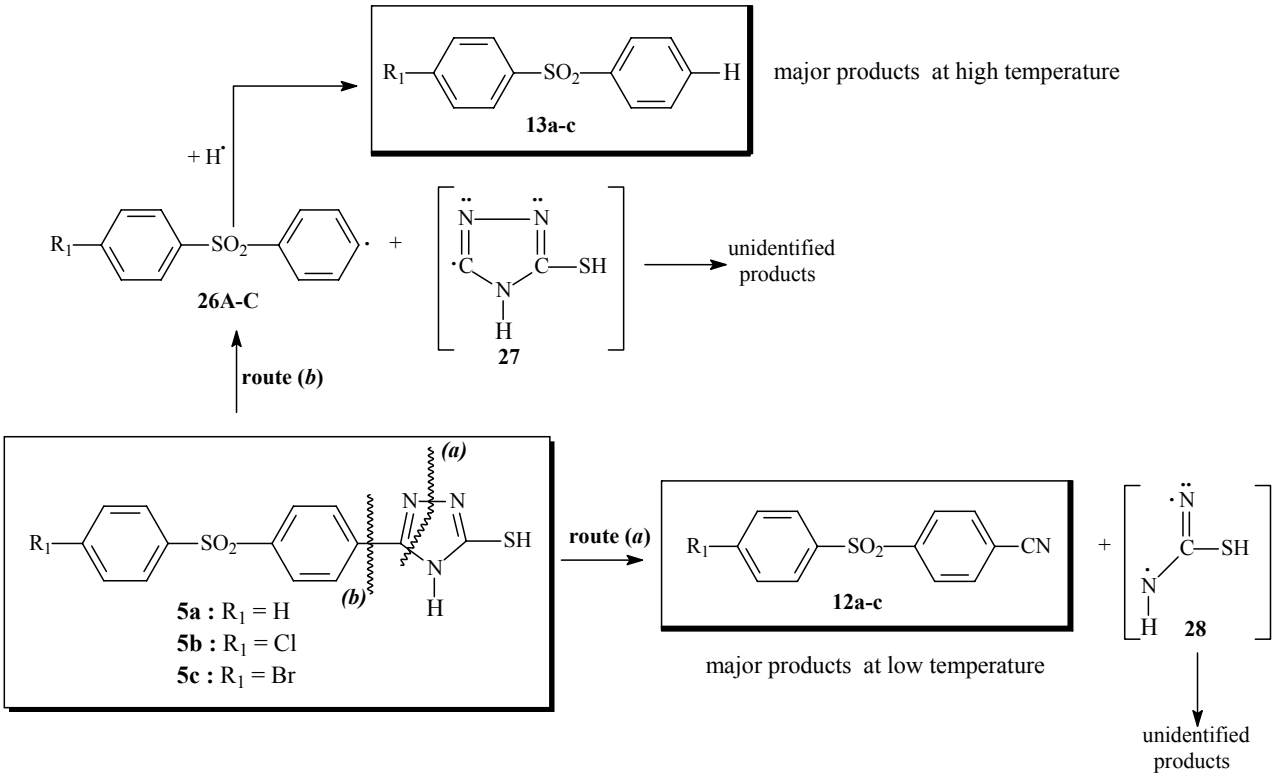
Examination of the data from Tables 1 – 3 suggests the following observations: the thermal decomposi-

tion of **5a-c** begins around 475^{0}C and ends at 750^{0}C; the higher concentration of the nitrile derivatives **12a-c** was obtained at low temperature and the main products at 750^{0}C are the corresponding diphenylsulphones **13a-c**.

A radical mechanism for rationalization of the experimental data is presented in Scheme 4.

The ***(a)*** route fragmentation involves the cleavage of N-N bond at low temperature with formation of the corresponding nitrile derivatives **12a-c** in the same manner with the literature's observations.[7,8]

The ***(b)*** route explains the formation of the diphenylsulfones **13a-c** as main products at 750^{0}C by cleavage of the triazole ring.



Scheme 4

In conclusion, this paper presents the thermal behavior in FVP conditions of three related 3-mercapto-5-substituted-1,2,4-triazoles between 475 – 750^{0}C.

At low temperature, the major reaction products are the corresponding cyano derivatives **12a-c** while at high temperature (750^{0}C) the corresponding diphenylsulfones **13a-c** are obtained.

The proposed radical reaction mechanism proves similar fragmentation routes of the all substituted 1,2,4-triazoles **5a-c**.

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