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RING-OPENING REACTION OF THE 1,3-DIAZETIDINE RING: HYDRAZINOLYSIS OF 2,4-BIS(HETEROARYLIMINO)-1,3-DIAZETIDINE DERIVATIVES

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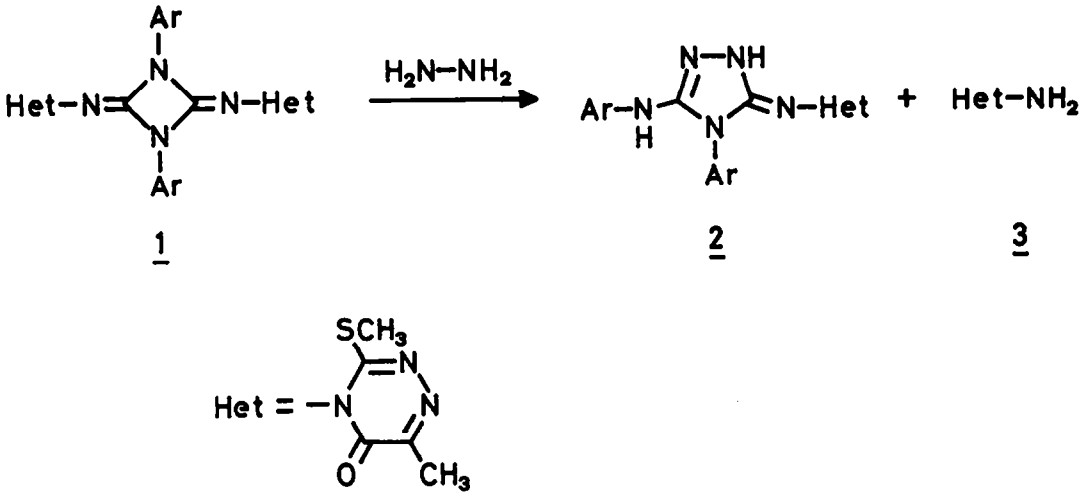
Abstract - *Reaction between 1,3-diaryl-2,4-bis(heteroarylimino)-1,3-diazetidines and anhydrous hydrazine yield 4-aryl-3-heteroarylimino-5-arylamino-2H-2,3-dihydro-1,2,4-triazoles. When methylhydrazine is used instead of hydrazine 1-methyl and, in some cases, 2-methyl derivatives were isolated. A tentative mechanism is proposed for the different compounds, which were fully characterized by mass spectrometry and ^{1}H and ^{13}C n.m.r. spectroscopy.*

The chemistry of the 2,4-diimino-1,3-diazetidines remains almost unexplored: it has been briefly mentioned that aryl carbodiimides dimerize to 1,3-diaryl-2,4-bis-(arylimino)-1,3-diazetidines in the presence of tributylphosphine[1]; for aliphatic carbodiimides reaction with alkylating agents such as dimethyl sulfate and trimethyloxonium tetrafluoroborate leads to N-alkyl-N-methyl-1,3-dialkyl-2-alkylimino-1,3-diazetidine-4-iminium salts, which are hydrolised with an excess of aqueous sodium hydroxide to give carbamoyl guanidines; however neutralization of the 1,3-diazetidine-iminium salts with bases leads to 1,3-dialkyl-2,4-bis(alkylimino)-1,3-diazetidines[2,3]. Dimerization of carbodiimides to 1,3-diazetidine derivatives has also been reported in the macrocyclic alkylene carbodiimide series[4]. Another method for the preparation of this type of compounds involves reaction of aryl isocyanide dichlorides with N,N',N''-triaryl guanidines[1] or amines[5,6].
Recently we have reported[7] that iminophosphorane derived from 4-amino-6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazine reacts with aryl isocyanates to give 1,3-diaryl-2,4-bis(heteroarylimino)-1,3-diazetidines which undergo hydrolytic cleavage to give 1,2,4-triazolo[5,1-c][1,2,4]triazine derivatives.

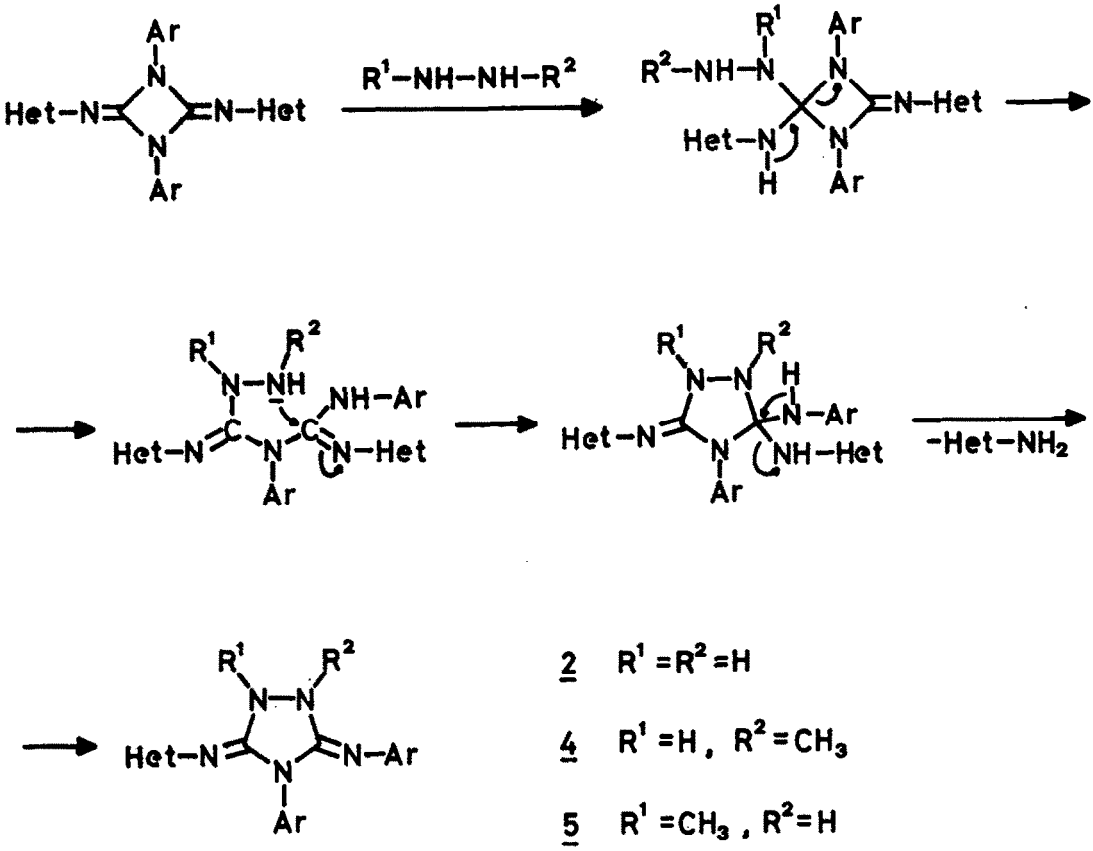
The high reactivity of the 1,3-diazetidine ring towards nucleophilic reagents prompted us to investigate the reaction of 1,3-diaryl-2,4-bis(heteroarylimino)-1,3-diazetidines 1 with hydrazine. Thus compounds 1 react with anhydrous hydrazine in dry dichloromethane at room temperature for 1 h to give the corresponding triazoles 2 in good yields (82-94%) and the N-aminoheterocycle 4-amino-6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazine 3.



1 2 3

Support for the formulation 2 is clearly provided by their microanalytical and spectral data. The i.r. spectra show absorptions in the region 1680-1670 cm^{-1} due to the carbonyl group in the 1,2,4-triazine ring. In the ^1H-n.m.r. spectra the chemical shifts of S-methyl and C-methyl groups are characteristic at δ 2.45-2.55 and δ 2.30-2.40 ppm respectively. Moreover, for 2a (Ar=C_6H_5) one phenyl group appears as a singlet which is characteristic of a phenyl-out-of-plane, and the other one appears as a multiplet. A similar situation is found in compounds 2d and 2e. In the mass spectra of compounds 2 the expected molecular ion peaks either appear in low intensity or are absent; the more significative peaks are due to the fragments M^+-157 and m/z 157, being the base peak the fragment at m/z 69.

We believe that the conversion 1 ⟶ 2 involves initial addition of one amino group of the reagent on the exocyclic C=N bond, followed by ring-opening to give an open-chain intermediate which undergoes cyclization and elimination of the heteroarylamine 3 to give 2.



2 $R^1 = R^2 = H$

4 $R^1 = H$, $R^2 = CH_3$

5 $R^1 = CH_3$, $R^2 = H$

According with this mechanism the reaction of 1 with methylhydrazine can yield two different triazoles 4 and 5 respectively. From the reaction of 1a (Ar=C_6H_5) with methylhydrazine in dry dichloromethane at room temperature only 4a is isolated as crystalline solid in moderate yield; under similar reaction conditions 1c (Ar= 4-$MeOC_6H_4$) leads to 4c in 33% yield; however, compound 1e (Ar=4-ClC_6H_4) gives a mixture of triazoles 4e and 5e in 48% and 21% yields respectively. In all the studied reactions the N-aminoheterocycle 3 is isolated as crystalline solid.

Support for the formulation 4 is based on its microanalytical and spectral data. The i.r. spectra show strong absorption band around 1670 cm^{-1} attributable to the carbonyl group. In the ^1H-n.m.r. spectra, the chemical shifts of the C-methyl, S-methyl and N-methyl groups are characteristic at δ 2.10-2.15, δ 2.50-2.55 and δ 3.60-3.85 ppm respectively. Mass spectra of compounds 4 show the expected molecular ion peak in high intensity, being the more significative peak due to the fragment [Ar-N=C=N-CH_3]. On the other hand, in the ^1H-n.m.r. spectrum of compound 5e the chemical shifts of the C-methyl, S-methyl and N-methyl groups are characteristic at δ 2.35, δ 2.45 and δ 3.45 ppm respectively; its mass spectrum shows the molecular ion peak and the fragment ion [Ar-N=C=N-Ar] does not appear.

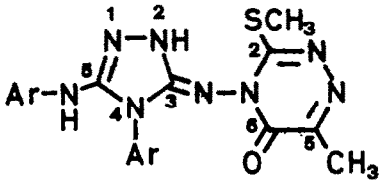
Table. Carbon-13 chemical shifts of triazoles **2**, **4** and **5**.

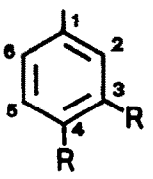
Compound No.	Triazole		Triazine			Ar-N_4	Ar-NH-C_5
	C_3	C_5	C_2	C_5	C_6		
2a Ar=$\overline{C}_6H_5$	150.5	145.3	160.2 13.7(SMe)	153.9 17.2(Me)	153.1	131.7(C_1),128.6($C_{2,6}$), 129.4($C_{3,5}$),129.1(C_4)	140.4(C_1),117.5($C_{2,6}$), 127.8($C_{3,5}$),121.2(C_4)
2b Ar=3-$\overline{MeO}C_6H_4$	150.4	145.1	160.2	154.0	152.9	132.5(C_1),113.7(C_2),159.8(C_3), 114.9(C_4),130.2(C_5),119.7(C_6), 54.8(OMe)	141.5(C_1),103.3(C_2),159.7(C_3), 106.8(C_4),129.4(C_5),109.9(C_6), 55.4(OMe)
2c Ar=4-$\overline{MeO}C_6H_4$	150.5	146.3	160.3 13.7(SMe)	154.1 17.1(Me)	153.2	124.0(C_1),129.3($C_{2,6}$), 114.7($C_{3,5}$),159.6(C_4),55.1(OMe)	133.2(C_1),119.7($C_{2,6}$), 113.8($C_{3,5}$),153.8(C_4),55.4(OMe)
2d Ar=3-$\overline{Cl}C_6H_4$	150.4	144.6	160.1 13.8(SMe)	154.0 17.2(Me)	152.8	132.7(C_1),129.4(C_2),133.1(C_3), 130.2(C_4),131.0(C_5),126.7(C_6)	141.6(C_1),117.1(C_2),133.5(C_3), 120.9(C_4),128.1(C_5),116.0(C_6)
2e Ar=4-$\overline{Cl}C_6H_4$	150.4	144.9	160.1 13.7(SMe)	154.0 17.2(Me)	152.8	130.3(C_1),129.8($C_{2,6}$), 129.6($C_{3,5}$),133.9(C_4)	139.0(C_1),119.1($C_{2,6}$), 128.4($C_{3,5}$),124.9(C_4)
2f Ar=1-Naphthyl	150.4	148.0	160.1 13.7(SMe)	153.8 17.2(Me)	154.2	134.0(C_1),122.8(C_2),127.8(C_3), 125.6(C_4),130.1(C_{4a}),129.7(C_5), 127.6(C_6),127.1(C_7),125.8(C_8) 127.3(C_{8a})	135.6(C_1),119.8(C_2),126.6(C_3), 122.5(C_4),133.7(C_{4a}),128.1(C_5), 125.5(C_6),125.3(C_7),122.8(C_8) 124.0(C_{8a})
4a[a] Ar=$\overline{C}_6H_5$	150.4	150.8	[b] 13.8(SMe)	152.1 16.7(Me)	152.1	140.2(C_1),128.7($C_{2,6}$), 128.5($C_{3,5}$),130.0(C_4)	144.2(C_1),118.0($C_{2,6}$), 127.7($C_{3,5}$),121.6(C_4)
4e[c] Ar=4-$\overline{Cl}C_6H_4$	150.4	149.0	159.7 13.9(SMe)	[b] 16.8(Me)	152.1	138.7(C_1),129.8($C_{2,6}$), 128.9($C_{3,5}$),135.0(C_4)	143.6(C_1),119.4($C_{2,6}$), 128.4($C_{3,5}$),125.3(C_4)
5e[d] Ar=4-$\overline{Cl}C_6H_4$	150.6	143.6	161.2 13.8(SMe)	154.4 17.0(Me)	153.4	129.8(C_1,129.5($C_{2,6}$), 129.4($C_{3,5}$),134.6(C_4)	137.6(C_1),122.5($C_{2,6}$), 128.7($C_{3,5}$),127.6(C_4)

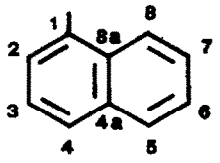
[a] 34.0 ppm (N-Me); [b] Not observed; [c] 33.9 ppm (N-Me); [d] 36.2 ppm (N-Me)

Carbon-13 n.m.r. study

The chemical shifts are collected in the Table. The assignment of the triazinone residue was made according to ref. 7. For the aryl groups, aromatic substituent effects[8] and reported values for 1-naphthylamine[9] were used.







Two main things differentiate both aryl groups: first, Ar-N_4 is an N-arylazole derivative[10] whereas Ar-NH-C_5 is a true aniline[8]; second, Ar-NH-C_5 is a planar conjugated system, whereas Ar-N_4 is an out-of-plane aryl[10] (see ^{1}H-n.m.r. before). Both criteria were used to assign the aromatic carbons to each aryl group. The assignment of C_3 and C_5 is complicated by the amino/imino tautomerism (vide infra). But, since one signal is insensitive (150.0 ± 0.1 ppm) to the Ar nature and the other clearly sensitive (144.6-148.0 ppm), the first one was assigned to C_3 and the second one to C_5.

Since methylation on N_1 (compounds 4a and 4e) modifies the chemical shift of C_5 (about 5 ppm), whereas that on N_2 (compound 5e) does not affect the C_3 chemical shift, we conclude that compounds 2 exist in DMSO-d_6 as depicted (3-heteroarylimino-5-arylamino), compounds 4 with both substituents in the imino form, and compound 5e like compound 2e. Normally[11] the diamino structure is favoured for guanazole, but the presence of the triazinone can shift the equilibrium towards the amino-imino tautomer.

EXPERIMENTAL

All melting points were determined using a Kofler hot-stage microscope and are uncorrected; i.r. spectra were recorded with a Nicolet FT 5DX spectrometer. ^{1}H-n.m.r. spectra were recorded at 60 MHz on a Varian EM-360A spectrometer using tetramethylsilane as internal standard. ^{13}C-n.m.r. spectra were recorded in DMSO-d_6 at 20 MHz on a Bruker WP-80SY spectrometer, unless compound 2f which was recorded at 75 MHz on a Varian XL-300 spectrometer. The chemical shifts of the Table are in ppm from tetramethylsilane. Mass spectra (70 eV) were obtained using a Hewlett-Packard 5993C instrument. Combustion analyses were performed with a Perkin-Elmer 240C instrument.

General Procedure for the Preparation of 4-aryl-5-arylamino-3-(6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazin-4-yl)imino-2H-2,3-dihydro-1,2,4-triazoles 2.

To a well-stirred solution of the appropriate 1,3-diaryl-2,4-bis(6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazin-4-ylimino)-1,3-diazetidine 1 (8 mmol) in dry dichloromethane (25 ml), anhydrous hydrazine (16 mmol) was added. The reaction mixture was stirred at room temperature for 1 h. The precipitated solid was collected by filtration and recrystallised from ethanol to give 2. Elimination of the solvent from the filtrate leads to a crude product which recrystallised from methanol gave 4-amino-6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazine 3. (m.p. 165°C; lit.[12] m.p. 165°C). The following derivatives 2 were obtained:

2a 4-Phenyl-5-phenylamino (94%), m.p. 189-191°C (yellow prisms). (Found: C 56.17; H 4.49; N 27.49. $C_{19}H_{18}N_8OS$ requires: C 56.14; H 4.46; N 27.57); i.r. (Nujol): 3300, 3100, 1670, 1627, 1596, 1585, 1557, 1500, 1330, 1313, 1296, 753, 736 and 690 cm^{-1}; δ (DMSO-d_6): 2.30 (s,3H), 2.50 (s,3H), 7.0-7.7 (m,5H), 7.75 (s,5H), 8.65 (s,1H); 12.10 (s,1H); m/z(%): 406 (M^+, 5), 251 (6), 250 (5), 157 (17), 116 (18), 110 (14), 93 (5), 77 (6), 74 (20), 69 (100), 48 (43), 47 (18), 46 (22), 45 (35),

43 (19).

2b 4-(m-Methoxyphenyl)-5-(m-methoxyphenyl)amino (82%), m.p. 190-192°C (yellow prisms). (Found: C 54.01; H 4.77; N 24.09. $C_{21}H_{22}N_8O_3S$ requires: C 54.07; H 4.75; N 24.02); i.r. (Nujol): 3285, 3070, 1676, 1647, 1608, 1588, 1556, 1490, 1329, 1308, 1284, 1228, 1193, 1165, 1050, 753 and 696 cm^{-1}; δ (DMSO-d_6): 2.30 (s,3H), 2.50 (s,3H), 3.80 (s,3H), 3.90 (s,3H), 6.5-8.0 (m,8H), 8.55 (s,1H), 12.00 (s,1H); m/z(%): 312 (12), 311 (41), 310 (27), 296 (10), 280 (11), 157 (42), 149 (11), 123 (11), 116 (33), 110 (28), 107 (10), 94 (11), 92 (12), 82 (10), 77 (12), 74 (25), 69 (100), 55 (13), 48 (46), 47 (26), 46 (19), 45 (27), 43 (16).

2c 4-(p-Methoxyphenyl)-5-(p-methoxyphenyl)amino (87%), m.p. 171-173°C (yellow prisms). (Found: C 54.12; H 4.78; N 23.98. $C_{21}H_{22}N_8O_3S$ requires: C 54.07; H 4.75; N 24.02); i.r. (Nujol): 3279, 3120, 1682, 1649, 1597, 1557, 1512, 1308, 1251, 1177, 1036, 832 and 679 cm^{-1}; δ (DMSO-d_6): 2.40 (s,3H), 2.55 (s,3H), 3.90 (s,3H), 4.05 (s,3H), 7.1-8.1 (m,8H), 8.45 (s,1H), 12.00 (s,1H); m/z(%): 360 (10), 312 (14), 311 (53), 310 (14), 309 (15), 297 (12), 296 (41), 294 (16), 269 (12), 254 (16), 157 (39), 149 (12), 148 (10), 123 (13), 116 (32), 110 (27), 108 (19), 107 (10), 94 (23), 92 (11), 74 (24), 69 (100), 48 (40), 47 (32), 46 (21), 45 (33).

2d 4-(m-Chlorophenyl)-5-(m-chlorophenyl)amino (87%), m.p. 216-217°C (yellow prisms). (Found: C 48.07; H 3.35; N 23.51. $C_{19}H_{16}N_8Cl_2OS$ requires: C 48.01; H 3.39; N 23.57); i.r. (Nujol): 3268, 3177, 3115, 3086, 1676, 1595, 1546, 1331, 1314, 906, 866, 787, 736 and 685 cm^{-1}; δ (DMSO-d_6): 2.30 (s,3H), 2.50 (s,3H), 6.9-7.7 (m,4H), 7.80 (s,4H), 8.90 (s,1H), 12.05 (s,1H); m/z(%): 476 (M^+, 8), 323 (5), 321 (15), 319 (21), 318 (9), 157 (33), 129 (7), 127 (15), 116 (29), 113 (7), 111 (19), 110 (23), 75 (12), 74 (24), 73 (11), 69 (100), 48 (31), 47 (18), 46 (15), 45 (21).

2e 4-(p-Chlorophenyl)-5-(p-chlorophenyl)amino (86%), m.p. 199-200°C (yellow prisms). (Found: C 47.93; H 3.41; N 23.62. $C_{19}H_{16}N_8Cl_2OS$ requires: C 48.01; H 3.39; N 23.57); i.r. (Nujol): 3273, 3194, 3131, 3103, 1676, 1648, 1591, 1551, 1495, 1313, 1240, 1087, 1013, 860, 832, 758 and 713 cm^{-1}; δ (DMSO-d_6): 2.30 (s,3H), 2.50 (s,3H), 7.2-7.8 (m,4H), 7.85 (s,4H), 8.80 (s,1H), 11.95 (s,1H); m/z(%): 328 (8), 321 (21), 320 (13), 319 (28), 318 (11), 157 (17), 154 (7), 152 (11), 129 (11), 127 (21), 116 (16), 113 (9), 111 (17), 110 (44), 99 (13), 94 (10), 82 (13), 79 (11), 75 (16), 74 (42), 69 (100), 48 (17), 46 (65), 45 (89).

2f 4-(1-Naphthyl)-5-(1-naphthyl)amino (92%), m.p. 205-206°C (yellow prisms). (Found: C 64.10; H 4.40; N 22.08. $C_{27}H_{22}N_8OS$ requires: C 64.02; H 4.38; N 22.12); i.r. (Nujol): 3280, 3100, 1682, 1653, 1602, 1574, 1512, 1421, 1397, 1330, 772 and 756 cm^{-1}; δ (DMSO-d_6): 2.35 (s,3H), 2.45 (s,3H), 6.7-7.7 (m,14H), 7.90 (s,1H), 11.30 (s,1H); m/z(%): 351 (6), 350 (10), 157 (40), 143 (6), 127 (5), 116 (40), 110 (23), 74 (20), 69 (100), 56 (8), 48 (24), 47 (16), 46 (12), 45 (19).

General Procedure for the Reaction of 1,3-Diaryl-2,4-bis(heteroarylimino)-1,3-diazetidines 1 with Methylhydrazine.

To a solution of the appropriate 1,3-diaryl-2,4-bis(heteroarylimino)-1,3-diazetidine **1** (8 mmol) in dry dichloromethane (25 ml), methylhydrazine (16 mmol) was added. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed off under reduced pressure and the resulting solid was treated with cold methanol. The solid was separated by filtration and recrystallised from methanol to give 4-amino-6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazine **3**. The mother liquors were kept at 0°C overnight and the precipitated solid was collected by filtration, dried and recrystallised from methanol to give **4**.
The following derivatives were obtained:

4a 1-Methyl-4-phenyl-5-phenylimino-3-(6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazin-4-yl)imino-2H-2,3-dihydro-1,2,4-triazole (40%), m.p. 245-246°C (yellow prisms). (Found: C 57.08; H 4.81; N 26.60. $C_{20}H_{20}N_8OS$ requires: C 57.13; H 4.79; N 26.65); i.r. (Nujol): 3296, 3183, 3126, 1672, 1636, 1595, 1561, 1540, 1496, 1450, 1332, 1313, 1289, 1264, 752, 703, 693, 672, 656 and 637 cm^{-1}; δ ($CDCl_3$): 2.10 (s,3H), 2.50 (s,3H), 3.70 (s,3H), 5.60 (s,1H), 7.1-7.8 (m,10H); m/z(%): 420 (M^+, 76), 379 (16), 305 (25), 292 (7), 278 (13), 265 (19), 264 (15), 249 (12), 222 (11), 195 (6), 180 (8), 132 (100), 131 (36), 118 (32), 117 (17), 104 (21), 92 (14), 91 (22), 77 (93).

4c 1-Methyl-4-(p-methoxyphenyl)-5-(p-methoxyphenyl)imino-3-(6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazin-4-yl)imino-2H-2,3-dihydro-1,2,4-triazole (33%), m.p. 193-194°C (yellow prisms). (Found: C 55.05; H 5.07; N 23.27. $C_{22}H_{24}N_8O_3S$ requires: C 54.99; H 5.03; N 23.32); i.r. (Nujol): 3205, 1670, 1653, 1597, 1551, 1512, 1331, 1308, 1257, 1178, 1030, 832, 815, 792, 758 and 725 cm^{-1}; δ ($CDCl_3$): 2.15 (s,3H), 2.50 (s,3H), 3.60 (s,3H), 3.85 (s,6H), 5.60 (s,1H), 6.7-7.6 (m,8H); m/z(%): 430 (M^+, 5), 326 (10), 325 (30), 311 (10), 310 (36), 157 (30), 156 (5), 147 (10), 116 (30), 110 (25), 74 (23), 69 (100).

4e **1-Methyl-4-(p-chlorophenyl)-5-(p-chlorophenyl)imino-3-(6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazin-4-yl)imino-2H-2,3-dihydro-1,2,4-triazole** (48%), m.p. 207-209°C (yellow prisms). (Found: C 49.02; H 3.68; N 22.96. $C_{20}H_{18}N_8Cl_2OS$ requires: C 49.09; H 3.71; N 22.90); i.r. (Nujol): 3307, 3279, 3183, 1678, 1648, 1597, 1568, 1546, 1495, 1331, 1308, 1246, 1093, 1036, 1013, 821, 759, 730, 709, 683 and 642 cm^{-1}; δ ($CDCl_3$): 2.15 (s,3H), 2.55 (s,3H), 3.60 (s,1H), 5.95 (s,1H), 7.40 (s,8H); m/z(%): 492 (M^++4, 17), 491 (20), 490 (M^++2, 74), 489 (29), 488 (M^+, 100), 449 (16), 447 (23), 374 (14), 372 (21), 335 (14), 333 (20), 332 (10), 319 (10), 168 (20), 166 (61), 165 (20), 153 (11), 152 (24), 151 (14), 127 (10), 111 (10), 99 (12).

From the reaction of **1e** (Ar= 4-Cl-C_6H_4) with methylhydrazine **2-methyl-4-(p-chlorophenyl)-5-(p-chlorophenyl)amino-3-(6-methyl-3-methylthio-5-oxo-4,5-dihydro-1,2,4-triazin-4-yl)imino-2H-2,3-dihydro-1,2,4-triazole** **5e** was also obtained in 21% yield as yellow prisms, m.p. 203-204°C . (Found: C 49.15; H 3.75; N 22.82. $C_{20}H_{18}N_8Cl_2OS$ requires: C 49.09; H 3.71; N 22.90); i.r. (Nujol): 3177, 1676, 1653, 1585, 1540, 1495, 1331, 1314, 1291, 1251, 1093, 1019, 833, 821, 763 and 717 cm^{-1}; δ (DMSO-d_6): 2.35 (s,3H), 2.45 (s,3H), 3.45 (s,3H), 6.8-7.6 (m,4H), 7.70 (s,4H), 8.95 (s,1H); m/z(%): 492 (M^++4, 5), 490 (M^++2, 7), 488 (M^+, 10), 337 (15), 336 (20), 335 (50), 334 (31), 333 (64), 332 (30), 319 (18), 317 (20), 263 (19), 162 (16), 157 (19), 155 (15), 153 (24), 127 (18), 116 (16), 11 (21), 74 (18), 69 (36), 48 (23), 46 (100), 45 (69).

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