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# CARBODIIMIDE-MEDIATED ANNELATION OF A [1,2,4]TRIAZOLE RING INTO A HETEROCYCLIC RING: SYNTHESIS OF [1,2,4]TRIAZOLO[4,3-b]-TRIAZOLE, IMIDAZO[1,2-b][1,2,4]TRIAZOLE AND [1,2,4]TRIAZOLO-[1,5-d][1,2,4]TRIAZINE DERIVATIVES

Pedro Molina*, Mateo Alajarín, Alicia Ferao, Angeles Lorenzo,
Mª Jesús Vilaplana, Enrique Aller, and José Planes

Departamento de Química Orgánica, Facultad de Ciencias,
Universidad de Murcia, Murcia 30001, Spain

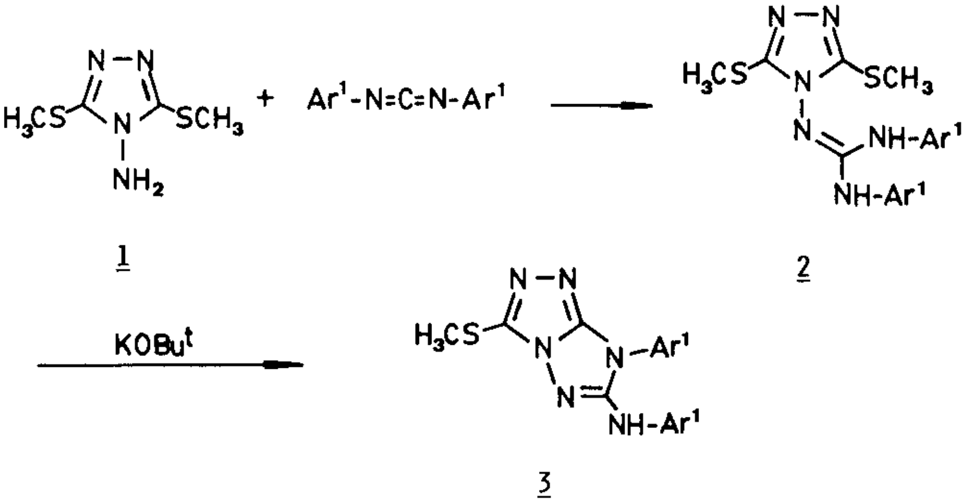
*Abstract* - *The N-aminoazoles 1 and 4 react with diarylcarbodiimides to give the corresponding N-guanidinoazoles which undergo base-catalyzed cyclization to give the fused [1,2,4]triazoles 3 and 6 respectively. The reactions of N-aminotriazines 7 and 8 with diarylcarbodiimides lead directly to the new triazolo-triazines 9 which display mesoionic character.*

As a part of an investigation on fused heterocycles, we have been engaged in the preparation of bridghead nitrogen heterocycles which contain the [1,2,4]triazolo moiety, e.g. [1,2,4]triazolo[1,5-a]pyridine[1], [1,2,4]triazolo[1,5-c]quinazoline[2], [1,2,4]triazolo[5,1-c][1,2,4]triazine[3], [1,2,4]triazolo[4,3-b][1,2,4]triazole[4], pyrazolo[5,1-c][1,2,4]triazole[5], [1,2,4]triazolo[3,4-b][1,3,4]thiadiazole[6], [1,2,4]triazolo[1,5-a]pyrazine[7], and [1,2,4]triazolo[3,4-b][1,3,4]thiadiazine[8]. In this context, we have briefly reported[9] that the reaction of functionalized N-aminoheterocycles with carbodiimides leads to fused [1,2,4]triazoles.

We now describe a general method for the preparation of some derivatives of the [1,2,4] triazolo[4,3-b][1,2,4]triazole ring system and of the otherwise not readily available imidazo[1,2-b][1,2,4]triazole and [1,2,4]triazolo[1,5-d][1,2,4]-triazine ring systems. Our approach is based on the reaction of the appropriate N-amino heterocycle, which is conveniently functionalized in at least one of the adjacent positions to the endocyclic nitrogen atom by a carbonyl, thiocarbonyl or methylthio group, whith diarylcarbodiimides to give N-heteroaromatic guanidines which undergo cyclization either by heating or in the presence of bases to give fused [1,2,4]triazoles. In the N-aminoazole series the presence of a thioiminoether group allows the preparation of neutral fused [1,2,4]triazoles, whereas *N*-aminoazines bearing a carbonyl or thiocarbonyl group lead to fused [1,2,4]triazoles which display mesoionic character.

## [1,2,4]Triazolo[4,3-b]triazoles

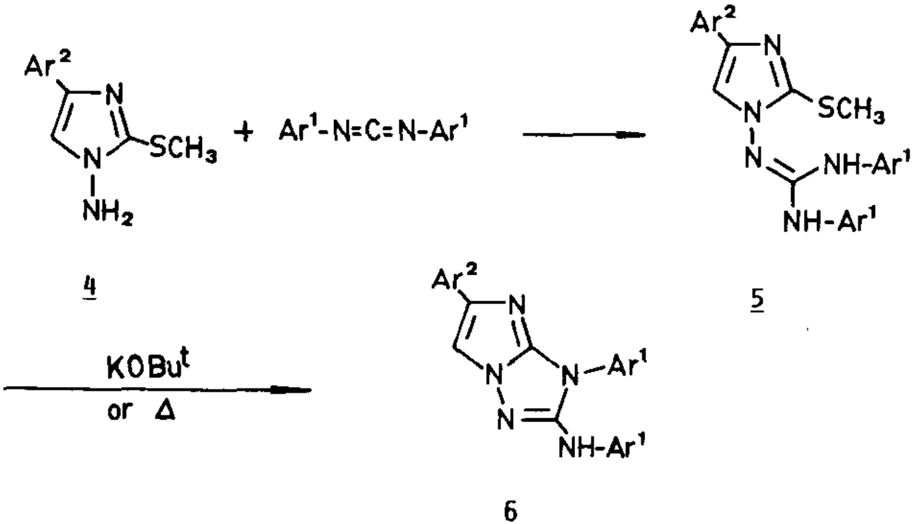
The *N*-aminoheterocycle 4-amino-3,5-bis(methylthio)[1,2,4]triazole **1**, readily available from thiocarbonohydrazide, carbon disulfide and methyl iodide[10], reacts with diarylcarbodiimides in dry toluene at reflux temperature for 60 h to give the corresponding 4-guanidino[1,2,4]triazoles **2** as crystalline solids in good yields (60-77%) (Table 1). The ir spectra of compounds **2** show a strong absorption band in the region 3415-3330 cm$^{-1}$ due to the NH group and at 1540-1515 cm$^{-1}$ attributable to the C=N bond. In the $^1$H-nmr spectra the chemical shift of the S-methyl groups is characteristic at $\delta$ 2.50 ppm. The mass spectra show the expected molecular ion peaks, and other significative is due to the fragment at *m/z* [Ar-N=C=N-Ar] . The 4-guanidino[1,2,4]triazoles **2** undergo base catalyzed cyclization by the action of potassium *t*-butoxide in *t*-butanol at reflux temperature for 48 h to give the corresponding [1,2,4]triazolo[4,3-*b*][1,2,4]-triazoles **3** as crystalline solids in moderate to excellent yields (50-94%) (Table 2). In the $^1$H-nmr spectra of compounds **3** the chemical shift of the S-methyl group is characteristic at $\delta$ 2.6-2.7 ppm, and one aryl group appears as a singlet which is characteristic of an out-of-plane aryl, whereas the other one appears as a multiplet. In addition, compound **3b** (Ar=4-$H_3C$-$C_6H_4$) shows two signals due to the two methyl groups on the benzene ring. Mass spectra show the expected molecular ion peaks in high intensity.



## Imidazo[1,2-b][1,2,4]triazoles

The methods described so far for the preparation of imidazo[1,2-*b*][1,2,4]-triazoles can be classified in two groups: a) from derivatives of the imidazole ring, e.g. phosphorus oxychloride-promoted dehydrative cyclization of 2-amino-

4-arylimidazoles[11]; and b) from derivatives of the [1,2,4]triazole ring, e.g. ring-closure of 1-phenacyl-5-amino[1,2,4]triazole with concentrated sulfuric acid[12,13]. We now report here an apparently widely applicable synthesis of 2-arylamino-3,5-diaryl-3*H*-imidazo[1,2-*b*][1,2,4]triazoles 6 in synthetically useful yields. Thus, *N*-aminoheterocycles 1-amino-2-methylthio-4-arylimidazoles 4, themselves readily available by condensation of isothiosemicarbazones derived from aromatic carbonyl compounds with phenacyl bromides and subsequent hydrazinolysis[14], react with diarylcarbodiimides in dry toluene at reflux temperature for 24 h to give the corresponding 1-guanidinoimidazoles 5 in good yields (60-87%) (Table 1). Compounds 5 undergo cyclization either by heating in dry toluene or by the action of potassium *t*-butoxide in *t*-butanol to give the desired 2-arylamino-3,5-diaryl-3*H*-imidazo[1,2-*b*][1,2,4]triazoles 6 as crystalline solids in good yields (65-76%) (Table 2). The ir spectra of compounds 5 show the typical bands due to the guanidino moiety and the $^1$H-nmr spectra show among others a signal as a singlet at $\delta$ 2.60 ppm due to the S-methyl group. Mass spectra of 5 show the expected molecular ion peaks, significative peaks are also found at *m/z* [Ar$^1$-N=C=N-Ar$^1$], [M$^+$ - CH$_3$SH], [Ar$^1$-NH-CN], [Ar$^2$-CN] and [Ar$^1$-NH$_2$]. Similarly, mass spectra of compounds 6 show the expected molecular ion peaks in high intensity and fragments at *m/z* [M$^+$ - Ar$^1$-NH-CN], [Ar$^1$-NH-CN] and [Ar$^2$-CN].



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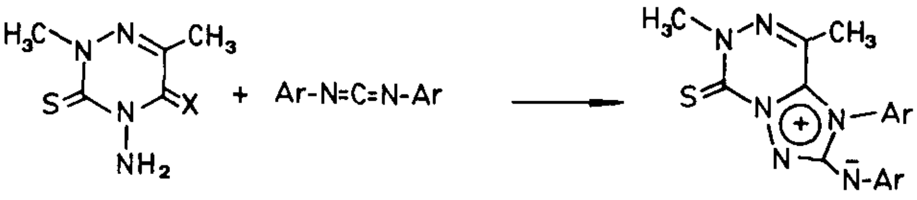
### [1,2,4]Triazolo[1,5-d][1,2,4]triazines

Only two methods have been reported for the synthesis of [1,2,4]triazolo[1,5-*d*]-[1,2,4]triazines: cyclization of 4-amino-5-imino[1,2,4]triazines with orthocarboxylates, acyl chlorides or carbonic acid anhydrides[15]; and, starting from 5-hydrazino[1,2,4]triazines, cyclization to [1,2,4]triazolo[4,3-*d*][1,2,4]-triazines and rearrangement to the isomeric [1,2,4]triazolo[1,5-*d*][1,2,4]-triazines[16]. We now describe here a new general method for the preparation of the unknown mesoionic derivatives of the [1,2,4]triazolo[1,5-*d*][1,2,4]triazine ring system from 4-amino[1,2,4]triazines and carbodiimides. The _N_-aminoheterocycle 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro[1,2,4]triazine _7_, readily available from *2-methylthiocarbonohydrazide and pyruvic* acid[17], reacts with diarylcarbodiimides in dry toluene at reflux temperature for 24 h to give directly the mesoionic 1-aryl-6,8-dimethyl-5-thioxo[1,2,4]triazolo[1,5-_d_][1,2,4]-triazylium-2-arylaminides _9_ as red solids in fair yields (59-69%). Similar *results can be achieved* from 4-amino-2,6-dimethyl-3,5-dithioxo-2,3,4,5-tetrahydro[1,2,4]triazine _8_, available from _7_ and phosphorus pentasulfide, under similar reaction conditions. Structural elucidation of _9_ is accomplished on the basis of spectral and microanalytical data. The ir spectra of all mesoionic derivatives _9_ show strong absorption bands in the region 1619-1560cm$^{-1}$ which can be attributed to C=N stretching; this wavenumber is similar to that reported for the monocyclic [1,2,4]triazolium-2-aminides[18]; in addition, the ir spectra show neither NH absorption bands nor a carbonyl stretching vibration (1676 cm$^{-1}$). The FAB-mass spectra show relatively abundant peaks at masses corresponding to the molecular ions but no significant fragment ions. The EI-spectra, obtained at sample temperatures of 210-215°C, show the expected molecular ion peaks and the fragmentation pattern is according with the proposed structure.



_7_ X=O
_8_ X=S

_9_

EXPERIMENTAL

Melting points were obtained on a Kofler hot-stage apparatus and are uncorrected. Ir spectra were run using NaCl plates on a Nicolet FT-5DX spectrophotometer in Nujol emulsions. $^1$H-Nmr spectra were obtained on a Varian FT-80 spectrometer at 80 MHz. The EI-mass spectra were obtained with a Hewlett-Packard 5993 C spectrometer. The FAB-mass spectra were determined on a Varian MAT 311 A instrument equipped with an Ion Tech FAB-11NF saddle field gun, using 8-9 kV argon atoms. Elemental analyses were performed with a Perkin Elmer 240 C instrument.

TABLE 1. Preparation of N-Guanidino Azoles 2 and 5.

| Entry | $Ar^1$ | $Ar^2$ | Mp(°C) | Yield (%) | Found C | Found H | Found N | Molecular Formula | Required C | Required H | Required N |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2a | $C_6H_5$ | | 214-216 | 77 | 55.16 | 4.92 | 22.61 | $C_{17}H_{18}N_6S_2$ | 55.11 | 4.89 | 22.68 |
| 2b | $4\text{-}H_3C\text{-}C_6H_4$ | | 222-224 | 63 | 57.35 | 5.52 | 21.03 | $C_{19}H_{22}N_6S_2$ | 57.26 | 5.56 | 21.08 |
| 2c | $4\text{-}Cl\text{-}C_6H_4$ | | 232-234 | 60 | 46.47 | 3.67 | 19.12 | $C_{17}H_{16}Cl_2N_6S_2$ | 46.46 | 3.66 | 19.13 |
| 2d | $4\text{-}Br\text{-}C_6H_4$ | | 224-226 | 70 | 38.53 | 2.95 | 18.71 | $C_{17}H_{16}Br_2N_6S_2$ | 38.64 | 3.06 | 18.89 |
| 5a | $C_6H_5$ | $C_6H_5$ | 177-179 | 87 | 69.29 | 5.18 | 17.41 | $C_{23}H_{21}N_5S$ | 69.15 | 5.30 | 17.53 |
| 5b | $4\text{-}H_3C\text{-}C_6H_4$ | $C_6H_5$ | 122-125 | 82 | 70.12 | 5.93 | 16.21 | $C_{25}H_{25}N_5S$ | 70.23 | 5.89 | 16.38 |
| 5c | $4\text{-}Cl\text{-}C_6H_4$ | $C_6H_5$ | 189-190 | 78 | 59.13 | 3.93 | 14.81 | $C_{23}H_{19}Cl_2N_5S$ | 58.98 | 4.09 | 14.95 |
| 5d | $C_6H_5$ | $4\text{-}Cl\text{-}C_6H_4$ | 115-116 | 62 | 63.58 | 4.71 | 16.19 | $C_{23}H_{20}ClN_5S$ | 63.66 | 4.64 | 16.14 |
| 5e | $4\text{-}H_3C\text{-}C_6H_4$ | $4\text{-}Cl\text{-}C_6H_4$ | 76-78 | 60 | 65.13 | 5.18 | 15.17 | $C_{25}H_{24}ClN_5S$ | 64.99 | 5.23 | 15.16 |
| 5f | $4\text{-}Cl\text{-}C_6H_4$ | $4\text{-}Cl\text{-}C_6H_4$ | 140-142 | 75 | 55.08 | 3.51 | 14.02 | $C_{23}H_{18}Cl_3N_5S$ | 54.94 | 3.61 | 13.93 |

TABLE 2. Preparation of Triazolotriazoles 3 and Imidazotriazoles 6.

| Entry | $Ar^1$ | $Ar^2$ | Mp(°C) | Yield (%) | Found C | Found H | Found N | Molecular Formula | Required C | Required H | Required N |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3a | $C_6H_5$ | | 97-99 | 50 | 59.53 | 4.51 | 25.91 | $C_{16}H_{14}N_6S$ | 59.61 | 4.38 | 26.07 |
| 3b | $4\text{-}H_3C\text{-}C_6H_4$ | | 106-108 | 69 | 61.54 | 5.22 | 23.81 | $C_{18}H_{18}N_6S$ | 61.70 | 5.17 | 23.98 |
| 3c | $4\text{-}Cl\text{-}C_6H_4$ | | 159-161 | 79 | 49.17 | 2.88 | 21.56 | $C_{16}H_{12}Cl_2N_6S$ | 49.11 | 3.08 | 21.48 |
| 3d | $4\text{-}Br\text{-}C_6H_4$ | | 134-136 | 94 | 39.82 | 2.61 | 17.48 | $C_{16}H_{12}Br_2N_6S$ | 40.04 | 2.52 | 17.50 |
| 6a | $C_6H_5$ | $C_6H_5$ | 181-183 | 65 | 75.23 | 4.98 | 19.77 | $C_{22}H_{17}N_5$ | 75.19 | 4.88 | 19.93 |
| 6b | $4\text{-}H_3C\text{-}C_6H_4$ | $C_6H_5$ | 197-198 | 72 | 76.08 | 5.43 | 18.31 | $C_{24}H_{21}N_5$ | 75.97 | 5.58 | 18.45 |
| 6c | $4\text{-}Cl\text{-}C_6H_4$ | $C_6H_5$ | 244-246 | 71 | 63.03 | 3.48 | 16.57 | $C_{22}H_{15}Cl_2N_5$ | 62.87 | 3.60 | 16.66 |
| 6d | $C_6H_5$ | $4\text{-}Cl\text{-}C_6H_4$ | 213-215 | 60 | 68.41 | 4.26 | 17.93 | $C_{22}H_{16}ClN_5$ | 68.48 | 4.18 | 18.15 |
| 6e | $4\text{-}H_3C\text{-}C_6H_4$ | $4\text{-}Cl\text{-}C_6H_4$ | 184-186 | 65 | 69.51 | 4.72 | 17.15 | $C_{24}H_{20}ClN_5$ | 69.64 | 4.87 | 16.92 |
| 6f | $4\text{-}Cl\text{-}C_6H_4$ | $4\text{-}Cl\text{-}C_6H_4$ | 255-257 | 76 | 57.92 | 3.18 | 15.32 | $C_{22}H_{14}Cl_3N_5$ | 58.11 | 3.10 | 15.40 |

4-Amino-2,6-dimethyl-3,5-dithioxo-2,3,4,5-tetrahydro[1,2,4]triazine 8. To a solution of 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro[1,2,4]triazine 7 (1.72 g, 10 mmol) in dry pyridine (40 ml), phosphorus pentasulfide (2.82 g) was added. The reaction mixture was stirred at reflux temperature for 5 h . After cooling, the solution was poured into ice-water (50 ml) and the precipitated solid was separated by filtration, dried and treated with hot ethanol (45 ml). The resultant solution was filtered and kept at 0°C overnight. The precipitated solid was collected by filtration and recrystallized from ethanol to give 8 (1.18 g, 63%) as yellow prisms, mp 150-151°C (Found: C, 31.83; H, 4.32; N, 29.63. $C_5H_8N_4S_2$ requires C, 31.89; H, 4.28; N, 29.75); Ir ν max. (Nujol) 3274, 3171, 1563, 1512, 1438, 1410, 1393, 1285, 1200, 1149, 1058, 787 cm$^{-1}$; $^1$H-nmr δ($CDCl_3$) 7.85 (2H,s,broad), 4.10 (3H,s), 2.60 (3H,s); m/z(%) 188(M$^+$, 100), 172(14), 159(11), 102(14), 99(12), 74(57), 73(15), 72(16), 70(12), 69(12), 45(14), 43(12), 42(13).

General Procedure for the Formation of 6-Arylamino-7-aryl-3-methylthio[1,2,4]-triazolo[4,3-b][1,2,4]triazoles 3. To a solution of 4-amino-3,5-bis(methylthio) [1,2,4]triazole 1 (1.76 g, 10 mmol) in dry toluene (50 ml) the appropriate diarylcarbodiimide (10 mmol) was added. The reaction mixture was stirred at reflux temperature for 60 h . After cooling, the precipitated solid was collected by filtration, dried and recrystallized from toluene to give 2 as colourless needles.

To a solution of the appropriate 4-(N,N'-diaryl)guanidino-3,5-bis(methylthio) [1,2,4]triazole 2 (2 mmol) in t-butanol (30 ml), potassium t-butoxide (4 mmol) was added. The resultant solution was heated under reflux with stirring for 48 h. After cooling, the solvent was removed under reduced pressure and the residual material was scratched with cold water (5 ml) and 1N hydrochloric acid was added until pH=7. The separated solid was collected by filtration, washed with water (3x30 ml), dried and recrystallized from ethanol/ether (1:1, v/v) to give 3 as white prisms.

General Procedure for the Formation of 2-Arylamino-3,5-diaryl-3H-imidazo[1,2-b]-[1,2,4]triazoles 6. *To a solution of the appropriate 1-amino-4-aryl-2-methylthio*imidazole 4 (10 mmol) in dry toluene (50 ml), the corresponding diarylcarbodiimide (10 ml) was added. The resultant solution was heated under reflux for 24 h . After cooling, the solution was concentrated to dryness under reduced pressure. The crude product was purified by recrystallization from dichloromethane/hexane (1:1, v/v) to give 5 as colourless needles.

To a solution of the appropriate 1-(N,N'-diaryl)guanidino-4-aryl-2-methylthioimidazole 5 (5 mmol) in t-butanol (60 ml), potassium t-butoxide (10 mmol) was added. The reaction mixture was heated under reflux for 24 h . After cooling, the solvent was removed under reduced pressure and the residual material was washed with water (3x30 ml), dried and recrystallized from dichloromethane/hexane (1:1, v/v) to give 6 as white needles.

Similar results were obtained when a solution of 5 in dry toluene was heated under reflux for 60 h .

TABLE 3. Spectral Data of Compounds 2, 3, 5 and 6.

| Compound No. | Ir ν (cm$^{-1}$) | $^{1}$H-Nmr$^{a}$ δ (ppm) | Ms$^{b}$ m/z (%) |
|---|---|---|---|
| 2a | 3330,1608,1589,1583,1537,1501,1450 1418,1358,1294,1230,1184,976,758,696,690. | 8.65(1H,s);<br>8.60(1H,s);<br>7.5-6.9(10H,m);<br>2.50(6H,s). | 370(M$^{+}$,26),322(15),195(29),194(100),93(34),91(13),77(36),65(18),51(26),45(25). |
| 2b | 3415,1608,1591,1580,1515,1441,1391,1308,1282,1244,1178,1022,985,970,818,804,789,748,706. | 8.42(1H,s);<br>8.33(1H,s);<br>7.4-6.8(8H,m);<br>2.50(6H,s);<br>2.20(6H,s). | 398(M$^{+}$,40),350(23),223(31),222(67),175(11),132(24),116(10),107(67),106(84),104(13),91(72),90(10),77(36),47(100),45(64). |
| 2c | 3393,1616,1595,1578,1537,1493,1415,1385,1352,1300,1242,1180,1093,1014,987,972,831,820,729. | 7.8-7.1(10H,m);<br>2.50(6H,s). | 442(M$^{+}$+4,2),440(M$^{+}$+2,7),438(M$^{+}$,11),266(5),264(31),262(49),240(21),184(17),161(49),152(47),73 127(54),111(49),102(47),73(48),47(59),45(100). |
| 2d | 3381,1614,1587,1578,1531,1487,1408,1346,1300,1284,1238,1178,1074,1011,985,872. | 9.00(1H,s);<br>8.90(1H,s);<br>7.7-7.0(8H,m);<br>2.50(6H,s). | 530(M$^{+}$+4,5),528(M$^{+}$+2,10),526(M$^{+}$,5),345(10),352(21),350(11),300(14),298(13),198(26),196(28),172(11),171(70),161(33),117(22),102(40),90(41),73(50),47(100). |
| 3a | 3358,1619,1597,1574,1546,1500,1336,1308,1251,1234,1189,1104,1081,1047,957,883,832,781,758,741,696. | 9.48(1H,s);<br>7.90(5H,s);<br>7.8-7.2(5H,m);<br>2.73(3H,s). | 322(M$^{+}$,100),220(43),204(13),195(8),180(12),161(22),129(13),118(15),104(10),7(8). |
| 3b | 3273,1600,1580,1557,1512,1330,1257,1234,1189,1104,1013,974,934,843,815,789,775,742,719. | 9.25(1H,s);<br>7.75(4H,s);<br>7.8-7.2(4H,m);<br>2.73(3H,s);<br>2.50(3H,s);<br>2.35(3H,s). | 350(M$^{+}$,36),248(15),218(49),208(31),175(37),143(38),132(100),131(41),118(72),106(20),91(82),77(23),65(34). |

Table 3 (Cont.)

| | | | |
|---|---|---|---|
| 3c | 3251,1614,1591,1574,1495,1404,1325,1245,1189,1098,1013,826,764,724. | 9.50(1H,s);<br>7.90(4H,s);<br>7.8-7.3(4H,m);<br>2.70(3H,s). | 394($M^+$+4,10),392($M^+$+2,48)390($M^+$,69),288(22),262(18),250(31),238(48),197(34),195(88),165(30),163(87),154(33),152(100),140(19),138(51),113(12),111(35). |
| 3d | 3262,1614,1603,1578,1553,1489,1400,1331,1238,1190,1107,1074,1012,843,821,764,715. | 9.60(1H,s);<br>8.1-7.1(4H,m);<br>7.65(4H,s);<br>2.71(3H,s). | 482($M^+$+4,5),480($M^+$+2,10),478($M^+$,5),300(19),298(21),230(19),228(18),198(51),196(51),173(28),171(43),157(30),155(31),117(31),90(40),73(100),45(94). |
| 5a | 3177,1642,1602,1585,1517,1490,1404,1302,1251,1121,1076,1030,968,894,747,736,690. | 8.85(1H,s);<br>8.60(1H,s);<br>7.9-7.0(16H,m);<br>2.60(3H,s). | 399($M^+$,13),352(26),351(100),281(14),254(11),235(10),233(81),205(8),195(27),190(25),175(12),157(5),118(11),103(71),93(5),77(10). |
| 5b | 3307,3183,3149,1638,1606,1583,1559,1542,1510,1419,1318,1251,1109,811,742,698. | 8.95(1H,s);<br>8.70(1H,s);<br>8.0-7.0(14H,m);<br>2.70(3H,s);<br>2.30(6H,s). | 427($M^+$,26),380(29),379(23),309(8),248(11),240(23),205(15),190(18),157(10),131(11),117(21),107(100),103(14),77(29). |
| 5c | 3183,3143,1640,1605,1589,1578,1545,1495,1414,1248,1179,1094,1013,895,822,741,708,698. | 9.05(1H,s);<br>8.80(1H,s);<br>8.0-7.0(14H,m);<br>2.60(3H,s). | 471($M^+$+4,5),469($M^+$+2,25),467($M^+$,35),234(3),233(8),232(31),154(4),153(2),152(14),139(27),138(10),137(100),103(13),102(32). |
| 5d | 3279,1649,1597,1568,1313,1232,1141,1093,1030,1013,838,753,725,690. | 8.90(1H,s);<br>8.70(1H,s);<br>8.1-7.1(15H,m);<br>2.65(3H,s). | 435($M^+$+2,5),433($M^+$,15),327(14),208(10),194(100),167(10),152(12),141(10),139(28),129(13),119(16),111(23),104(19),93(38),77(71),55(45). |
| 5e | 3300,3170,1625,1602,1559,1540,1511,1092, | 8.75(1H,s);<br>8.50(1H,s); | 463($M^+$+2,4),461($M^+$,12),414(5),224(5),223(3),207 |

Table 3 (Cont.)

| | | | |
|---|---|---|---|
| | 1013,939,832,815,<br>724,690. | 8.1-7.1(13H,m);<br>2.60(3H,s);<br>2.30(6H,s). | (3),152(6),150(15),137<br>(8),132(15),117(100),107<br>(14),106(28),91(39),77<br>(21),65(21). |
| 5f | 3302,1635,1616,1595,<br>1574,1558,1493,1240,<br>1092,1013,826,724. | 8.0-7.4(13H,m);<br>6.15(2H,s);<br>2.60(3H,s). | 505($M^+$+4,2)503($M^+$+2,6),<br>501($M^+$,7),457(10),455(3),<br>453(35),268(20),267(21),<br>266(61),236(11),185(12),<br>152(34),151(12),150(18),<br>139(38),138(21),137(100). |
| 6a | 3132,1602,1585,1547,<br>1490,1326,1239,1116,<br>941,756,710. | 9.15(1H,s);<br>8.1-7.1(16H,m). | 351($M^+$,87),233(82),175<br>(12),118(12),116(15),103<br>(100),91(5),77(10). |
| 6b | 3234,1602,1574,1540,<br>1512,1240,1155,1019,<br>809,764,696. | 9.05(1H,s);<br>8.0-7.1(14H,m);<br>2.45(3H,s);<br>2.30(3H,s). | 379($M^+$,80),247(48),232<br>(6),189(11),132(14),117<br>(100),116(61),106(7),104<br>(6),90(30),77(15),65(13). |
| 6c | 3198,1605,1590,1571,<br>1543,1287,1094,1016,<br>826,773,707. | 9.30(1H,s);<br>8.3-7.2(14H,m). | 421($M^+$+2,14),419($M^+$,22),<br>268(7),232(62),152(17),<br>139(36),137(100),116(13),<br>111(6),102(16),77(5). |
| 6d | 3205,3058,1602,1574,<br>1546,1501,1451,1350,<br>1314,1268,1155,1039,<br>1013,838,752,723,<br>690. | 9.20(1H,s);<br>8.3-7.1(15H,m). | 387($M^+$+2,3),385($M^+$,9),267<br>(5),194(5),150(9),137<br>(22),118(13),111(5),103<br>(100),102(8),92(5),91(9),<br>77(24),65(7),51(16). |
| 6e | 3222,1602,1574,1540,<br>1512,1234,1193,1155,<br>1087,1036,1019,832,<br>809,724. | 8.95(1H,s);<br>8.2-7.2(13H,m);<br>2.45(3H,s);<br>2.30(3H,s). | 415($M^+$+2,38),413($M^+$,100),<br>150(11),137(8),132(19),<br>117(56),106(10),91(31),77<br>(15),69(14),65(18). |
| 6f | 3218,1603,1595,1574,<br>1546,1495,1342,1240,<br>1093,1013,826,730. | 9.40(1H,s);<br>8.4-7.5(13H,m). | 457($M^+$+4,3),455($M^+$+2,9),<br>453($M^+$,9),268(6),267(5),<br>266(17),152(21),139(29),<br>137(100),111(13),102(32). |

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[a] Obtained as solutions in DMSO-$d^6$, except for compounds 3a-3d which were recorded in $CDCl_3$. [b] Recorded at 70 eV.

General Procedure for the Formation of 1-Aryl-6,8-dimethyl-5-thioxo[1,2,4]triazolo[1,5-d][1,2,4]triazylium-2-arylaminides 9. To a solution of 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro[1,2,4]triazine 7 (0.86 g, 5 mmol) in dry toluene (40 ml), the appropriate diarylcarbodiimide (5 mmol) was added. The reaction mixture was stirred at reflux temperature for 24 h . After cooling, the red precipitated solid was collected by filtration, washed with hot toluene (4x10 ml), dried and recrystallized from nitrobenzene to give 9 as red-orange needles.

1-Phenyl-6,8-dimethyl-5-thioxo[1,2,4]triazolo[1,5-d][1,2,4]triazylium-2-phenylaminide (9a) (1.04 g, 60%) as red-orange needles, mp 290°C (Found: C, 61.91; H, 4.43; N, 24.32. $C_{18}H_{16}N_6S$ requires C, 62.05; H, 4.63; N, 24.12); Ir ν max. (Nujol) 1619, 1580, 1546, 1489, 1381, 1268, 1206, 1132, 1093, 1008, 866, 764, 730, 690 $cm^{-1}$; m/z(%) 349(26), 348($M^+$, 100), 289(36), 273(12), 232(16), 216(46), 119(19), 103(34), 91(13), 77(32).

1-(3-Chlorophenyl)-6,8-dimethyl-5-thioxo[1,2,4]triazolo[1,5-d][1,2,4]triazylium-2-(3-chlorophenyl)aminide (9b) (1.43 g, 69%) as red-orange needles, mp 298°C (Found: C, 51.57; H, 3.43; N, 20.29. $C_{18}H_{14}Cl_2N_6S$ requires C, 51.80; H, 3.38; N, 20.14); Ir ν max. (Nujol) 1619, 1581, 1545, 1481, 1389, 1281, 1211, 1140, 1074, 911, 866, 781, 758, 730, 690 $cm^{-1}$; m/z(%) 420($M^+$ + 4, 7), 418($M^+$ + 2, 50), 416($M^+$, 72), 252(4), 250(12), 218(6), 217(14), 216(100), 139(12), 137(40), 127(8), 111(22), 102(12), 73(16).

1-(4-Chlorophenyl)-6,8-dimethyl-5-thioxo[1,2,4]triazolo[1,5-d][1,2,4]triazylium-2-(4-chlorophenyl)aminide (9c) (1.28 g, 62%) as red-orange needles, mp 302°C (Found: C, 51.73; H, 3.18; N, 20.33. $C_{18}H_{14}Cl_2N_6S$ requires C, 51.80; H, 3.38; N, 20.14); Ir ν max. (Nujol) 1619, 1585, 1546, 1489, 1279, 1206, 1138, 1087, 1002, 832, 758, 724, 696 $cm^{-1}$; m/z(%) 420($M^+$ + 4, 10), 418($M^+$ + 2, 50), 416($M^+$, 72), 252(6), 250(12), 217(16), 216(100), 139(14), 137(42), 127(10), 111(22), 102(12), 73(10).

1-(4-Bromophenyl)-6,8-dimethyl-5-thioxo[1,2,4]triazolo[1,5-d][1,2,4]triazylium-2-(4-bromophenyl)aminide (9d) (1.86 g, 66%) as red-orange needles, mp 311°C (Found: C, 42.61; H, 2.85; N, 16.51. $C_{18}H_{14}Br_2N_6S$ requires C, 42.71; H, 2.79; N, 16.60); Ir ν max. (Nujol) 1619, 1580, 1557, 1489, 1285, 1161, 1138, 1070, 1019, 991, 832, 758, 724, 696 $cm^{-1}$; m/z(%) 508($M^+$ + 4, 8), 506($M^+$ + 2, 14), 504($M^+$, 8), 451(50), 449(100), 447(50), 369(30), 367(30), 312(16), 310(16), 210(26), 173(38), 171(44), 157(28), 155(28), 102(24), 71(32), 42(28).

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