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Heterocumulene-Mediated Annelation of a [1,3,4]Thiadiazine or [1,3,4]Oxadiazine Ring into an Imidazole Ring: Preparation and Crystal Structure of Some Derivatives of the Unknown Imidazo[1,5-*d*]-[1,3,4]thiadiazine and Imidazo[1,5-*d*][1,3,4]oxadiazine Ring Systems.

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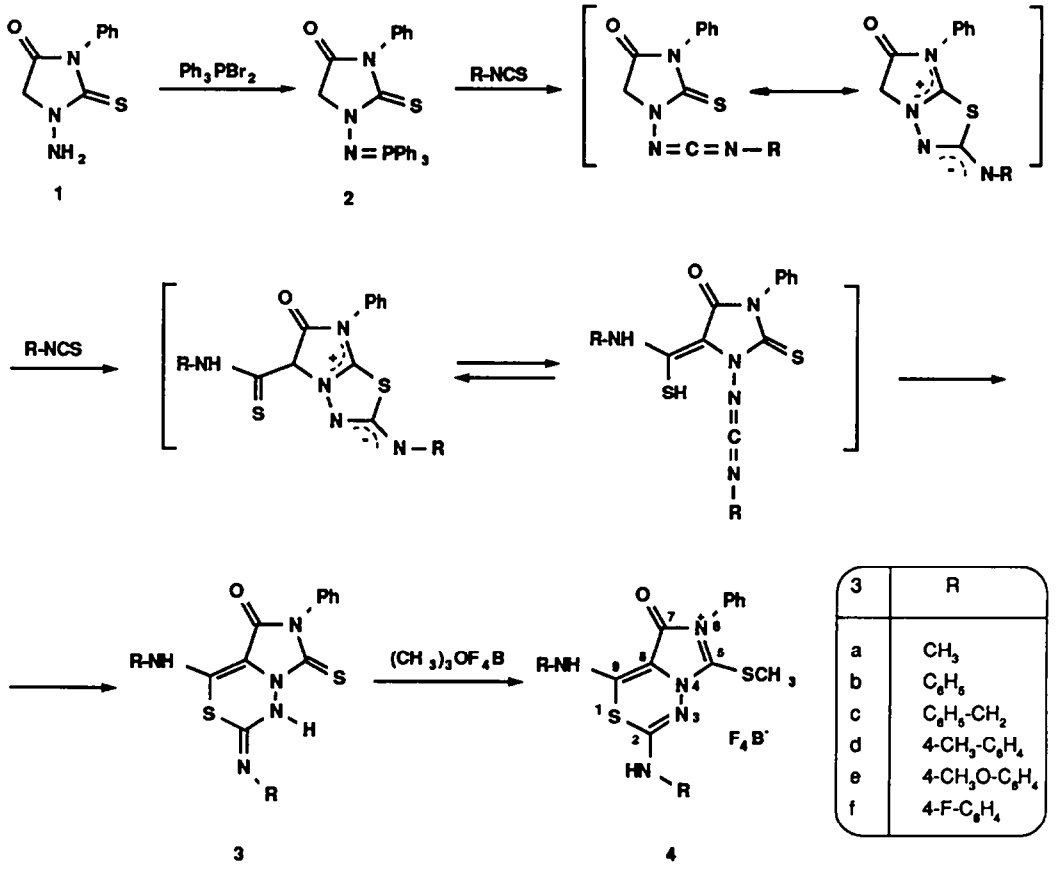
Abstract— The aza-Wittig reaction of iminophosphorane **2** derived from 1-amino-3-phenyl-2-thioxo-4-imidazolidinone **1** with heterocumulenes leads to fused imidazoles. Iminophosphorane **2** reacts under mild conditions with isothiocyanates to form imidazo[1,5-*d*]-[1,3,4]thiadiazines **3** which undergo S-methylation to give imidazo[1,5-*d*][1,3,4]thiadiazinium salts **4**. Iminophosphorane **2** also reacts with isocyanates under mild conditions to give imidazo[1,5-*d*][1,3,4]oxadiazines **5**. The N-aminoheterocycle **1** by the action of diaryl carbodiimides undergoes ring-closure/ring-opening reaction to give the corresponding [1,2,4]triazoles **7**, which by sequential treatment with trimethyloxonium tetrafluoroborate and triethylamine/methanol are converted into the oxygen analog **9**. The crystal structure of the hydrated salt **4a** has been solved by X-Ray diffraction methods. The two independent cations form dimers that pack in chains along the b axis through hydrogen interactions, in such a way that all anions and solvent molecules (H_2O and 2 $HCCl_3$ in the asymmetric unit) are located in the unit cell into two channels which are described.

The imidazole ring plays an essential role in several biological processes. Accordingly a massive research effort has been expended on the chemistry of this ring, and also on condensed derivatives[1]. As a part of an investigation on the synthesis of fused heterocycles from N-aminoheterocycles[2], in particular, of bridgehead-nitrogen heterocycles containing the imidazo moiety, we recently reported the synthesis of [5+5] and [5+6] fused imidazoles[3].

We now describe a general method for the preparation of some derivatives of the previously unreported imidazo[1,5-*d*][1,3,4]thiadiazine and imidazo[1,5-*d*][1,3,4]oxadiazine rings, under completely neutral conditions, based on the ready synthesis and subsequent aza-Wittig type reaction of iminophosphorane derived from 1-amino-3-phenyl-2-thioxo-4-imidazolidinone **1** with heterocumulenes.

The N-aminoheterocycle **1**, readily available from phenyl isothiocyanate and ethyl hydrazinoacetate[4], reacts with triphenylphosphine dibromide to give the iminophosphorane **2** as crystalline solid in 60% yield. Aza-Wittig reaction of iminophosphorane **2** and several isothiocyanates in dry methanol at room temperature leads to the corresponding imidazo[1,5-*d*][1,3,4]thiadiazines **3** as the only product in 40-54% yields. Upon reaction with trimethyloxonium tetrafluoroborate at room temperature in dry dichloromethane compounds **3** gave 2,9-bis(arylamino)-5-methylthio-7-oxo-6-phenylimidazo[1,5-*d*][1,3,4]thiadiazin-



3	R
a	CH_3
b	C_6H_5
c	C_6H_5-CH_2
d	4-CH_3-C_6H_4
e	4-CH_3O-C_6H_4
f	4-F-C_6H_4

Scheme 1

6-ium tetrafluoroborates **4** in near quantitative yields (Scheme 1).

The first indication of a structure type **3** is obtained from ^1H and ^{13}C-NMR spectra which clearly show that there are two groups of signals for the alkyl or aryl residue; in addition, in the ^1H-NMR the signal corresponding to the methylene protons at position 5 of the imidazolidinone ring is absent. In order to identify unambiguously the structure of the reaction product X-ray structure determination of crystalline compound **4a** has been performed.

The main geometrical parameters are shown in Table A, according to the numbering system[5] given in Fig. 1. There are no significant differences between both cations (see experimental part) except those involving the conformation of the C19 methyl groups (bond angles at C5 and N6-C5-S10-C19 torsion angle). No reference was found in the Cambridge Structural Database (CSD, July 1989 release, 73893 entries)[6] for the bicycle and just 1[7] and 16 hits[8-23] were located when this moiety was split in the corresponding six and five-membered rings. The main differences (lowest bond distances than the corresponding mean values) are those involving the N4-C5-N6 fragment, where the positive charge seems to be located for the present compound. Moreover, the carbonyl conjugated double C8-C9 bond

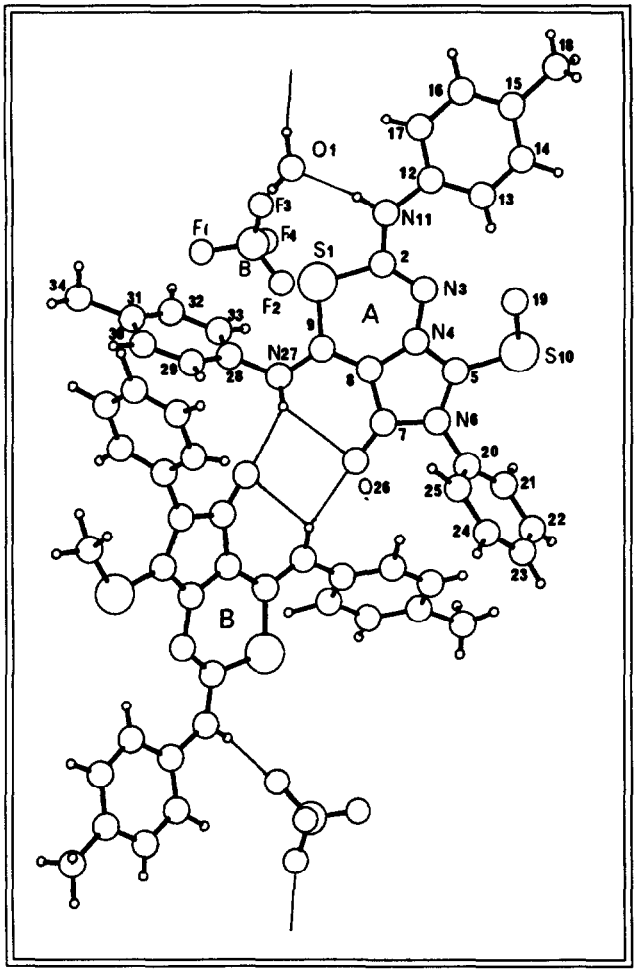


Fig. 1. *A view of the hydrated salt **4a** showing the hydrogen interactions and the numbering system.*

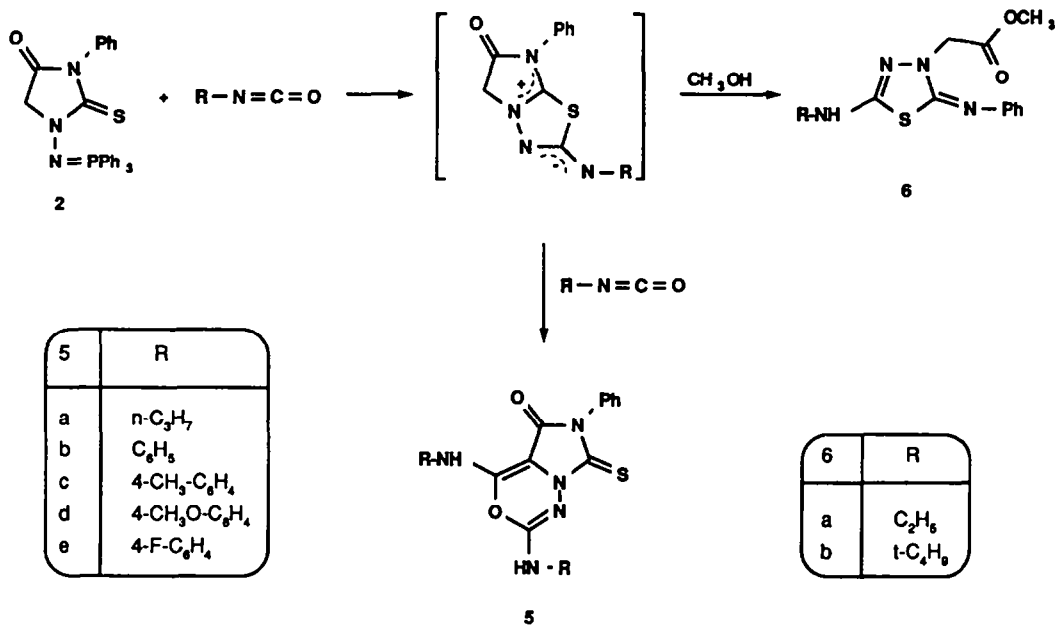
is delocalized, since this bond length is longer and those of its neighbours shorter than the expected ones. The above mentioned rings makes angles of 3.5(3) and 2.2 (3)°, in molecules A and B respectively. The N27-H27...O26 intramolecular interactions, in both molecules, could contribute to the planarity of the bicycle (see Table A). Both independent cationic moieties are held together by N-H..O=C hydrogens bonds, and they are related by a pseudobinary axis, almost parallel to the c axis and passing through (0.239, 0.239, 0.076). The crystal is built by chains (along the b axis) of dimers, joined through BF_4^- and water molecules by N-H..O, O-H..F and N-H..F hydrogen bonds (see Table A and Fig. 1). All the anions and solvent molecules (H_2O and $HCCl_3$) are located in the unit cell into two channels, which are described in Fig. 2. They consist roughly in two cilinders, centrosimmetrically related, centered around the helicoidal axis at (1/4, y, 1/4) and at (3/4, y, 3/4) of approximate transverse dimensions of 3.5 x 4.5Å in average. The cilinder sections are elliptical and modulated (see Fig. 2) as to give sections with a "cactus-like" shape at x=1/4 (Fig. 2, (a)) and a distorted "hourglass" shape at z=1/4 (Fig. 2, (b)). The holes resembling the cactus arms form about 40° with respect to the helicoidal axis. The two channels are touching each other at y=0.40 (and symmetry related sections). The approximate dimensions and shapes of the sections are:

-- At y=1/2, it is ellipsoidal (centered at 0.285, 1/2, 0.267 and with axis of 6.5 and 5.2Å) with an adjacent small circle (centered at 0, 1/2, 0.225 and diameter of 2.5Å). Moreover, in this section it appears the hole of a cactus arm (centered at 1/4, 0.300, 1/2 and with dimensions of 4.7 and 11.0Å approximately).

-- At y=1/4 it becomes in just an ellipsoid (centered 0.245, 1/4, 0.459 and dimensions of 5.5 and 11.2Å).

Since ^{1}H-NMR spectrum of compound **3a** (R=Me) shows an methyl group as a doublet (J=1.1 Hz) and the other one as a singlet and no signal for a methine proton is present, we conclude that compound **3a** exists in DMSO-d_6 as despicted (2-methylamino-9-methylimino). This fact is also observed for compound **3c** (R=Ph-CH_2).

Presumably the conversion **2**→**3** involves initial aza-Wittig type reaction between the iminophosphorane **2** and the isothiocyanate to give a carbodiimide as highly reactive intermediate which spontaneously cyclizes to the bicyclic mesoionic compound, which reacts with a second molecule of

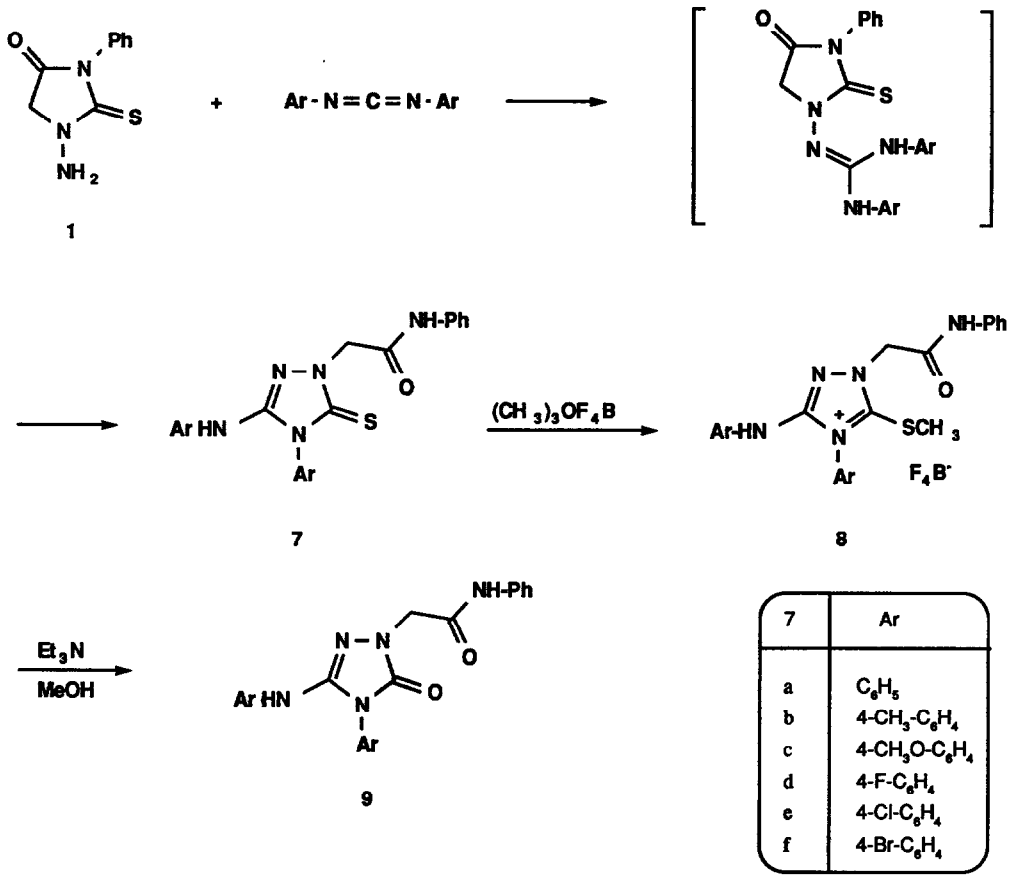


Scheme 2

isothiocyanate. Ring opening of the 1,3,4-thiadiazole ring and subsequent ring closure by nucleophilic attack of the thiocarboxamide group on the electrophilic sp-hybridized carbon atom of the carbodiimide moiety leads to **3**. The thiocarbamoylation at position 5 of the imidazolidinone ring is an unprecedented reaction, to the best of our knowledge.

Similarly, the reaction of iminophosphorane **2** with isocyanates in dry methanol leads to the corresponding imidazo[1,5-*d*][1,3,4]oxadiazines **5** in moderate yields 40-51%. However, compound **2** reacts with ethyl and t-butylisocyanate to give the 1,3,4-thiadiazoles **6** as only reaction products in 47-56% yields. The formation of compounds **6** can be understood as ocurring by initial aza-Wittig type reaction between iminophosphorane **2** and the isocyanate to give the corresponding bicyclic mesoionic compound as intermediate which undergoes ring opening of the imidazolidinone ring by nucleophilic attack of methanol on the carbonyl group to give **6** (Scheme 2). In the ^{1}H-NMR spectrum of compound **6a** (R=C_2H_5), the N-methylene protons appears as a complex multiplet which suggests an exocyclic NH group at position 5. On the other hand, the N-aminoheterocycle **1** reacts with diarylcarbodiimides in dry toluene at reflux temperature for 24 h to give the corresponding 1-substituted 4-aryl-3-arylamino-5-thioxo-4,5-dihydro[1,2,4]triazoles **7** in 42-55% yields. Presumably, the **1**→**7** transformation involves initial addition of the amino group on the carbodiimide to give an heteroaryl guanidine and subsequent cyclization by intramolecular nucleophilic attack of the nitrogen atom of the guanidine group on the thiourea moiety of the five-membered ring and concomitant ring-opening of the imidazolidinone would give **7**.

Compounds **7** undergo S-methylation by the action of trimethyloxonium tetrafluoroborate to give the salts **8** in high yields 66-89% which by treatment with triethylamine in methanol are converted into the 1,2,4-triazoles **9** in 67-92% yields (Scheme 3). The ^{13}C-NMR study of compounds **7** shows that both aryl



7	Ar
a	C_6H_5
b	4-CH_3-C_6H_4
c	4-CH_3O-C_6H_4
d	4-F-C_6H_4
e	4-Cl-C_6H_4
f	4-Br-C_6H_4

Scheme 3

TABLE A. Selected geometrical parameters (Å, °). I=(x, y+1, z)

	Mol. A	Mol. B		Mol. A	Mol. B		Mol. A	Mol. B
S1-C2	1.769(9)	1.769(9)	C9-N27	1.321(10)	1.328(11)	N6-C7	1.401(10)	1.417(11)
C2-N3	1.297(11)	1.286(11)	S10-C19	1.767(14)	1.683(19)	C7-O26	1.225(10)	1.208(10)
N4-C8	1.400(10)	1.395(10)	S10-C19'	1.605(52)	—	C8-C9	1.374(11)	1.386(11)
C5-N6	1.382(11)	1.373(11)	S1-C9	1.751(8)	1.746(8)	N11-C12	1.426(11)	1.432(11)
N6-C20	1.453(11)	1.441(11)	N3-N4	1.381(9)	1.370(9)	N27-C28	1.414(10)	1.427(11)
C7-C8	1.436(11)	1.428(12)	N4-C5	1.311(10)	1.321(10)	S10-C5	1.719(8)	1.716(9)
C2-N11	1.352(11)	1.340(11)						
C9-S1-C2	101.1(4)	100.8(4)	N3-N4-C5	120.8(7)	119.6(7)	N6-C7-C8	105.0(7)	103.5(7)
C2-N3-N4	116.0(7)	116.8(7)	C8-C9-N27	123.7(7)	121.5(7)	S1-C2-N11	109.2(6)	110.9(6)
N4-C8-C9	125.6(7)	122.8(7)	C2-N11-C12	129.9(7)	129.2(7)	N4-C5-S10	126.2(7)	120.6(6)
C8-N4-C5	111.6(7)	111.3(7)	C5-S10-C19	103.7(6)	110.4(6)	C7-N6-C20	124.4(7)	121.9(7)
C5-N6-C7	109.8(6)	110.9(7)	C5-S10-C19'	121.7(18)	—	C8-C7-O26	129.8(7)	130.2(8)
C7-C8-N4	105.7(6)	107.1(7)	S1-C2-N3	130.7(7)	130.0(7)	C7-C8-C9	128.7(7)	129.9(8)
N3-C2-N11	120.1(7)	119.1(8)	N3-N4-C8	127.6(6)	129.1(7)	S1-C9-N27	117.5(6)	118.2(6)
C5-N6-C20	125.7(7)	127.1(7)	C8-C9-S1	118.8(6)	120.4(6)	C9-N27-C28	124.8(7)	125.8(7)
N6-C7-O26	125.3(7)	126.4(8)	N4-C5-C6	107.9(7)	107.3(7)	N6-C5-S10	125.9(6)	132.1(6)

	Mol. A	Mol. B		Mol. A	Mol. B
S1-C2-N11-C12	176(1)	176(1)	S1-C9-N27-C28	1(1)	2(1)
C2-N11-C12-C13	10(1)	11(1)	C9-N27-C28-C29	-124(1)	-126(1)
C5-N6-C20-C21	-72(1)	-77(1)	O26-C7-C8-C9	1(1)	6(2)
C7-C8-C9-N27	4(1)	-2(1)	C8-C9-N27-H27	14(7)	19(6)
N6-C5-S10-C19	-128(1)	-7(1)	N6-C5-S10-C19'	6(2)	—

N11A..O1	2.844(10)	H11A..O1	2.02(8)	N11A-H11A..O1	172(7)
N27A..O26A	3.021(9)	H27A..O26A	2.40(9)	N27A-H27A..O26A	133(8)
N27A..O26B	2.946(9)	H27A..O26B	2.22(9)	N27A-H27A..O26B	146(8)
N27B..O26B	3.020(9)	H27B..O26B	2.42(7)	N27B-H27B..O26B	125(6)
N27B..O26A	3.008(9)	H27B..O26A	2.18(8)	N27B-H27B..O26A	154(7)
N11B..F1B	2.869(12)	H11B..F1B	2.01(8)	N11B-H11B..F1B	169(7)
O1..F3A	2.83(3)	H1..F3A	2.04(16)	O1-H1..F3A	147(14)
O1..F3'A	2.88(6)	H1..F3'A	2.02(17)	O1-H1..F3'A	159(14)
O1..F3B(i)	2.85(1)	H2..F3B(i)	2.13(18)	O1-H2..F3B(i)	153(16)
C25B..Cl1B	3.63(1)	H25B..Cl1B	2.86(10)	C25B-H25B..Cl1B	148(9)
CA..Cl2B	3.85(2)	HA..Cl2B	3.01(—)	CA-HA..Cl2B	142(—)

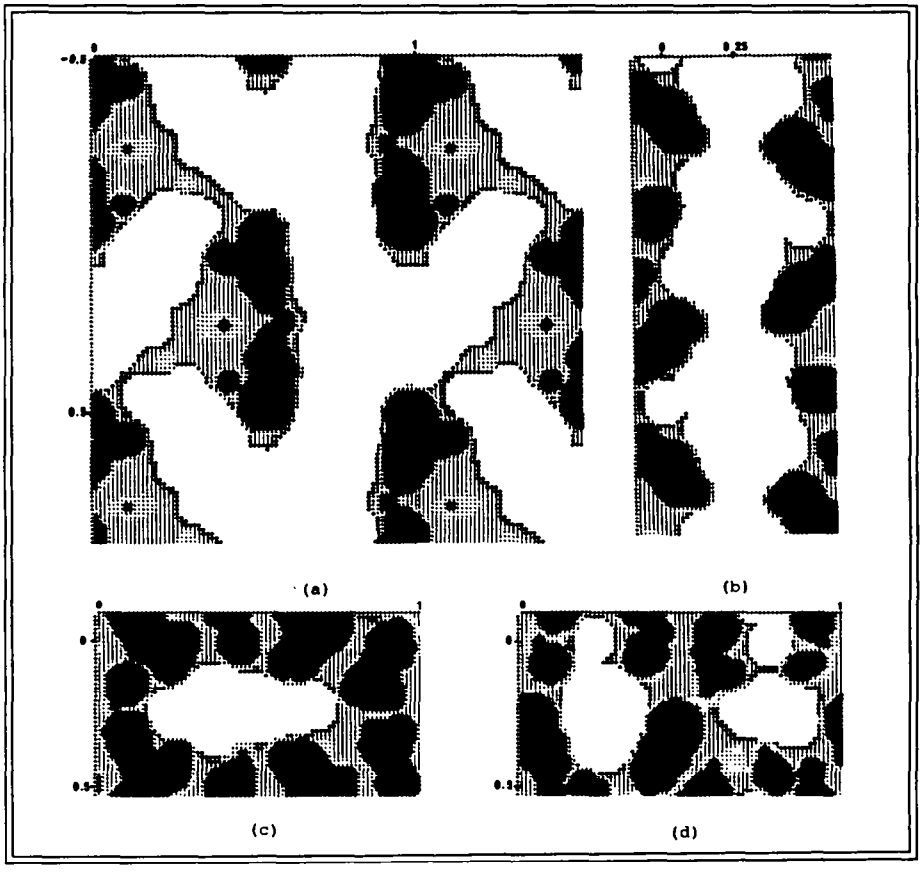


Fig. 2.
The continous channel (two in the unit cell) that hold inside the anions and the solvent molecules. Sections through: (a) x=0.25, (b) z=0.25, (c) y=0.25 and (d) y=0.50.

A 0.25Å grid for the holes search and a rolling sphere of radius 1.4Å was used for smoothing the cations clefts which are drawn in grey, while the van der Waals interior of atoms appear in dark[25].

groups at position 3 and 4 are differents: the Ar-N_4 is an N-arylazole derivative whereas Ar-NH-C_3 is a true aniline[24].

In conclusion, the results presented here confirm that the unknown imidazo[1,5-*d*][1,3,4]thiadiazine and imidazo[1,5-*d*][1,3,4]oxadiazine ring systems may be prepared under mild conditions by a new heterocumulene-mediated annelation strategy.

TABLE B. FINAL ATOMIC COORDINATES

	Molecule A			Molecule B		
S1	0.2781(1)	0.4696(1)	0.0308(1)	0.1939(1)	0.0083(1)	0.0189(1)
C2	0.3757(5)	0.4931(4)	0.0573(4)	0.1009(5)	-0.0171(4)	0.0539(5)
N3	0.4335(4)	0.4601(3)	0.0861(4)	0.0447(4)	0.0158(3)	0.0833(4)
N4	0.4183(4)	0.3956(3)	0.0973(3)	0.0575(4)	0.0807(3)	0.0905(3)
C5	0.4724(5)	0.3581(4)	0.1269(4)	0.0040(5)	0.1164(4)	0.1238(4)
N6	0.4432(4)	0.2959(3)	0.1260(3)	0.0329(4)	0.1783(3)	0.1251(4)
C7	0.3668(5)	0.2949(4)	0.0946(4)	0.1089(5)	0.1819(4)	0.0921(4)
C8	0.3495(5)	0.3610(4)	0.0779(4)	0.1236(5)	0.1172(4)	0.0699(4)
C9	0.2809(5)	0.3869(4)	0.0489(4)	0.1911(5)	0.0903(4)	0.0390(4)
S10	0.5649(1)	0.3817(1)	0.1582(2)	-0.0826(2)	0.0828(1)	0.1559(2)
N11	0.3856(4)	0.5565(3)	0.0436(4)	0.0916(4)	-0.0808(3)	0.0464(4)
C12	0.4518(5)	0.5977(4)	0.0589(4)	0.0282(5)	-0.1214(4)	0.0713(4)
C13	0.5256(6)	0.5778(4)	0.0831(5)	-0.0428(6)	-0.0990(4)	0.0992(6)
C14	0.5848(5)	0.6223(5)	0.0983(5)	-0.0989(5)	-0.1418(5)	0.1248(5)
C15	0.5725(5)	0.6882(4)	0.0885(5)	-0.0867(6)	-0.2068(5)	0.1211(6)
C16	0.4992(6)	0.7066(4)	0.0639(5)	-0.0183(8)	-0.2283(5)	0.0908(8)
C17	0.4386(5)	0.6629(4)	0.0480(5)	0.0392(6)	-0.1871(5)	0.0653(6)
C18	0.6384(6)	0.7357(5)	0.1039(6)	-0.1499(8)	-0.2527(6)	0.1481(10)
C19	0.5426(9)	0.4445(7)	0.2187(7)	-0.1340(11)	0.1370(7)	0.2042(12)
C19'	0.6309(33)	0.3304(24)	0.1838(29)	—	—	—
C20	0.4834(5)	0.2398(4)	0.1556(5)	-0.0035(5)	0.2335(4)	0.1586(5)
C21	0.5483(7)	0.2154(5)	0.1227(6)	-0.0655(7)	0.2646(6)	0.1292(6)
C22	0.5848(9)	0.1615(7)	0.1502(8)	-0.0994(9)	0.3174(7)	0.1668(7)
C23	0.5561(10)	0.1329(6)	0.2097(10)	-0.0691(9)	0.3366(6)	0.2282(8)
C24	0.4906(10)	0.1576(7)	0.2412(8)	-0.0080(10)	0.3073(7)	0.2575(7)
C25	0.4529(7)	0.2121(6)	0.2151(7)	0.0279(7)	0.2529(6)	0.2231(7)
O26	0.3254(3)	0.2468(3)	0.0860(3)	0.1491(4)	0.2298(3)	0.0846(3)
N27	0.2157(4)	0.3531(3)	0.0347(4)	0.2550(4)	0.1257(3)	0.0237(4)
C28	0.1444(5)	0.3785(4)	0.0048(5)	0.3261(5)	0.1032(4)	-0.0102(5)
C29	0.0736(5)	0.3705(4)	0.0404(5)	0.3991(6)	0.1145(5)	0.0228(5)
C30	0.0023(6)	0.3936(5)	0.0118(6)	0.4674(6)	0.0946(5)	-0.0124(6)
C31	0.0017(6)	0.4259(4)	-0.0535(6)	0.4661(6)	0.0634(5)	-0.0771(6)
C32	0.0733(6)	0.4337(4)	-0.0882(5)	0.3927(7)	0.0520(5)	-0.1075(5)
C33	0.1442(5)	0.4099(4)	-0.0612(5)	0.3218(6)	0.0726(5)	-0.0757(5)
C34	-0.0764(6)	0.4518(6)	-0.0845(7)	0.5432(8)	0.0424(7)	-0.1118(8)
Cl1	0.3719(2)	0.5819(2)	0.2357(2)	0.2360(4)	0.3051(3)	0.2276(3)
Cl2	0.2527(3)	0.6554(3)	0.1609(3)	0.1732(4)	0.4250(4)	0.2219(3)
Cl3	0.2152(3)	0.5989(4)	0.2945(2)	0.3388(4)	0.4031(4)	0.2724(3)
C	0.2713(10)	0.5927(9)	0.2185(8)	0.2397(10)	0.3771(9)	0.2743(8)
F1	0.1593(5)	0.5087(6)	-0.2243(5)	0.2220(6)	-0.1519(4)	-0.0143(6)
F2	0.2765(13)	0.4705(12)	-0.1799(12)	0.3430(7)	-0.1895(7)	0.0194(9)
F2'	0.2281(40)	0.4591(23)	-0.2228(29)	—	—	—
F3	0.2410(13)	0.5671(11)	-0.1724(17)	0.2501(11)	-0.2505(5)	-0.0117(11)
F3'	0.2735(39)	0.5273(45)	-0.1500(18)	—	—	—
F4	0.2764(8)	0.5214(10)	-0.2793(7)	0.2419(10)	-0.1996(12)	0.0821(8)
F4'	0.2593(22)	0.5669(22)	-0.2524(26)	—	—	—
B	0.2396(8)	0.5178(7)	-0.2124(7)	0.2672(11)	-0.1976(9)	0.0147(12)
O1	0.2540(4)	0.6132(3)	-0.0304(4)	—	—	—

(pp(F2)=pp(F3)=pp(F4)=0.71(2), pp(F2')=pp(F3')=pp(F4')=0.29(2), pp(C19)=0.79(2), pp(C19')=0.21(2); pp = Population parameter)

EXPERIMENTAL SECTION

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. I.R. spectra were obtained as Nujol emulsions on a Nicolet FT-5DX spectrophotometer. NMR spectra were recorded on a Bruker AC-200 (200 MHz). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer. Microanalyses were performed on a Perkin-Elmer 240C instrument.

X-Ray Crystallography.- Table B shows the final atomic coordinates for the non-hydrogen atoms. Table C displays the crystal data and experimental parameters at room temperature. There are two independent ionic pairs, two $HCCl_3$ solvent and a water molecules within the asymmetric unit. The highest temperature factors correspond to the BF_4^- (mol. B), to the $HCCl_3$ groups and to the C19 (mol. B) atom. The BF_4^- (mol. A) group appears to be disordered between two positions, remaining fixed the B and F1 atoms. The F3 and F3' atoms are involved in hydrogen interactions with the water molecule. In spite of the high temperature factors several attemps to find a disordered model for the other BF_4^- group and for the $HCCl_3$solvent molecules were unsuccessful. C19 (mol. A) atom also appears disordered, showing two different conformations with respect to the N6 atom. The conformation displayed by molecule B corresponds to that with the lowest population parameter in molecule A. The hydrogen atoms of these methyl groups could not be located. Some hydrogen parameters, namely those of H191, H192, H193, H22 and H32 atoms (mol. B), had to be kept fixed in the last cycle of refinement.

3-Phenyl-2-thioxo-1-triphenylphosphoranylidenamino-4-imidazolidinone (2).

A solution of bromine (2.39 g, 15 mmol) in dry benzene (40 ml) was added dropwise to a stirred solution of triphenylphosphine (3.98 g, 15 mmol) in dry benzene (40 ml) at 0°C under nitrogen. The mixture was stirred for 1 h then allowed to stand at room temperature for 30 min. A solution of 1-amino-3-phenyl-2-thioxo-4-imidazolidinone **1** (3.10 g, 15 mmol) and triethylamine (3.03 g, 30 mmol) in dry benzene (20 ml), was added and the mixture was heated to reflux for 16 h, whereupon a solid precipitates, which was separated by suction from the warm solution, slurried with anhydrous ethanol (3x20 ml) and filtered. The crude product was recrystallized from ethanol/benzene (1:1) to give **2** (60%) as white prisms, m.p. 201-202°C. (Found: C, 69.16; H, 4.83; N, 9.18. $C_{27}H_{22}N_3OSP$ requires : C, 69.36; H, 4.74; N, 8.99); i.r. (Nujol): 1748, 1738, 1501, 1487, 1291, 1195, 1161, 1121, 1104, 1047, 996, 957, 832, 752, 729 and 718 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 4.09 (d, 2H, J=2.1 Hz), 7.09(dd, 2H, J=7.9, J=1.9 Hz), 7.32-7.50 (m, 3H), 7.51-7.65 (m, 9H), 7.77 (ddd, 6H, J=11.5, J=7.7 and J=1.4 Hz); ^{13}C n.m.r. δ (DMSO-d_6) 57.70 (CH_2), 128.04, 128.24 (J=93.2 Hz), 128.41, 128.68, 128.79 (J=11.5 Hz), 132.58 (J=2.7 Hz), 132.88 (J=9.2 Hz), 134.17, 168.63 (C=O), 178.14 (J=8.1 Hz, C=S); m/z (%) : 467 (M^+, 5), 262 (8), 201 (10), 192 (30), 185 (31), 183 (74), 135 (77), 119 (13), 109 (10), 108 (19), 107 (19), 93 (15), 91 (16), 77 (100).

General Procedure for the Preparation of 9-Alkyl(aryl)amino-2-alkyl(aryl)imino-7-oxo-6-phenyl-5-thioxo-3H-imidazo[1,5-*d*][1,3,4]thiadiazines (3).

To a well-stirred suspension of iminophosphorane **2** (0.93 g, 2 mmol) in anhydrous methanol (10 ml) was added the appropriated isothiocyanate (4 mmol). The resultant solution was stirred at room temperature for 6 h. Then, the precipitatd solid was separated by filtration and slurried with cold methanol (3x10 ml) and filtered. The crude product was recrystallized from methanol to give **3**. The following derivatives **3** were obtained:

(3a) 9-Methylamino-2-methylimino (42%), m.p. 273-275°C (yellow prisms). (Found: C, 48.72; H,

TABLE C. Crystal analysis parameters at room temperature.

Crystal data	
Formula	$(C_{26}H_{24}N_5S_2O\ BF_4.HCCl_3)_2.H_2O$
Crystal size (mm)	0.53 x 0.23 x 0.13
Symmetry	Monoclinic, $P2_1/n$
Unit cell determination:	Least-squares fit from 87 reflexions ($\theta < 42°$)
Unit cell dimensions	16.6913(10), 20.7720(18), 18.6869(13) Å
	90, 90.347(7), 90°
Packing: V(Å^3), Z	6478.8(8), 4
Dc(g/cm^3), M, F(000)	1.441, 1405.65, 2880
μ(cm^{-1})	42.911
Experimental data	
Technique	Four circle diffractometer: Philips PW1100
	Bisecting geometry
	Graphite oriented monochromator: CuKα
	$\omega/2\theta$ scans, scan width: 1.5°
	Detector apertures 1° x 1°, up θ max. 60° 0.8 min./reflex.
Number of reflexions:	
Independent	8913
Observed	4954 (3 σ (I) criterion)
Standard reflexions:	2 reflexions every 90 minutes.
	No variation.
Max-min transmission	
factors:	0.728, 1.389
Solution and refinement	
Solution	Direct Methods for Difference Structures.
Refinement	L. S. on F_{obs} with 6 blocks.
Parameters:	
Number of variables	994 (See text)
Degrees of freedom	3960
Ratio of freedom	5.0
H atoms	Difference synthesis
Final shift/error	0.13
w-scheme	Empirical as to give no trends in $<\omega\Delta^2F>$
	vs. $<\|F_{obs}\|>$ and $<\sin\theta/\lambda>$
Max. thermal value	U_{22}(F 4 B)=0.44(3) Å^2
Final DF peaks	0.96 e/Å^3 near to $HCCl_3$ group.
Final R and Rw	0.087, 0.103
Computer and programs	MicroVax 3200, XRAY80[26], DIRDIF[27], DIFABS[28].
Scattering factors	Int. Tables for X-Ray Crystallography[29].

4.25; N, 22.16. $C_{13}H_{13}N_5OS_2$ requires: C, 48.88; H, 4.10; N, 21.92); i.r. (Nujol): 3239, 1682, 1642, 1585, 1552, 1494, 1308, 1268, 1195, 1165, 1132, 1087, 1013, 928, 747, and 730 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+DMSO-d_6): 2.97 (d, 3H, J=1.1 Hz, CH_3-NH-), 3.08 (s, 3H, CH_3-N=), 7.34-7.47 (m, 5H, aryl), 7.94 (s, 1H, NH), 8.22 (s, broad, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+DMSO-d_6): 29.48 (CH_3), 30.36 (CH_3), 95.57, 127.99, 128.40, 128.51, 133.67, 141.60, 144.57, 156.43 (C=O), 160.07 (C=S); m/z (%): 319 (M^+, 39), 286 (6), 200 (10), 136 (29), 135 (98), 119 (25), 101 (10), 100 (75), 91 (19), 77 (100), 74 (73).

(3b) 9-Phenylamino-2-phenylimino (46%), m.p. 220-221°C (yellow prisms). (Found: C, 62.12; H, 3.97; N, 15.73. $C_{23}H_{17}N_5OS_2$ requires: C, 62.30; H. 3.84; N, 15.80); i.r. (Nujol) : 3217, 1693, 1670, 1648, 1631, 1597, 1552, 1501, 1319, 1144, 1093, 866, 764, 747, and 730 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+DMSO-d_6): 7.00 (t, 1H, J=7.4 Hz), 7.24-7.49 (m, 12H), 7.83 (d, 2H, J=7.9 Hz), 9.33 (s, 1H, NH), 9.60 (s. broad, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+DMSO-d_6): 97.67, 119.09, 122.54, 124.27, 126.76, 127.89, 128.03, 128.24, 128.30, 129.03, 132.71, 135.49, 137.78, 138.97, 139.09, 156.89 (C=O), 162.74 (C=S); m/z (%): 443 (M^+, 5), 411 (4), 324 (5), 136 (14), 135 (100), 119 (18), 118 (25), 104 (11), 93 (16), 91 (18), 77 (70).

(3c) 9-Benzylamino-2-benzylimino (40%), m.p. 169-171°C (yellow prisms). (Found: C, 63.51; H, 4.63; N, 14.71. $C_{25}H_{21}N_5OS_2$ requires: C, 63.67; H. 4.49; N, 14.85); i.r. (Nujol) : 3466, 3313, 1685, 1643, 1600, 1538, 1489, 1442, 1353, 1301, 1149, 1117, 1057, 1028, 959, 743, 736, and 723 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+DMSO-d_6): 4.50 (d, 2H, J=1.3 Hz, Ar-CH_2-NH), 4.57 (s, 2H, Ar-CH_2-N=), 7.24-7.47 (m, 15H), 7.99 (t, 1H, J=1.3 Hz, NH), 8.74 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+DMSO-d_6): 46.45 (CH_2), 47.17 (CH_2), 96.08, 126.63, 126.94, 127.33, 127.75, 127.87, 128.11, 128.28, 128.36, 128.43, 133.59, 137.13, 137.73, 140.76, 143.09, 156.20 (C=O), 160.40 (C=S); m/z (%): 471 (M^+, 5), 149 (15), 138 (10), 132 (8), 119 (5), 106 (15), 91 (100), 77 (15).

(3d) 9-(4-Tolylamino)-2-(4-tolylimino) (54%), m.p. 244-245°C (yellow prisms). (Found: C, 63.79; H, 4.69; N, 14.61. $C_{25}H_{21}N_5OS_2$ *requires*: C, 63.69; H, 4.45; N, 14.86); *i.r. (Nujol)*: 3477, 3375, 1687, 1653, 1616, 1534, 1512, 1325, 1217, 1149, 1093, 810, and 742 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+DMSO-d_6): 2.25 (s, 3H, Ar-CH_3), 2.34 (s, 3H, Ar-CH_3), 7.07 (d, 2H, J=8.4 Hz), 7.22 (s, 4H), 7.32-7.53 (m, 5H), 7.73 (d, 2H, J=8.4 Hz), 9.54 (s, 1H, NH), 9.93 (s, broad, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+DMSO-d_6): 19.97 (CH_3), 20.18 (CH_3), 97.47, 118.71, 124.72, 127.70, 128.02, 128.05, 128.62, 129.26, 131.29, 133.02, 133.26, 136.40, 136.78, 137.88, 138.89, 155.98 (C=O), 162.28 (C=S); m/z (%): 471 (M^+, 5), 380 (4), 352 (5), 150 (15), 149 (100), 135 (23), 132 (19), 131 (15), 119 (8), 106 (8), 91 (79), 77 (21).

(3e) 9-(4-Methoxyphenylamino)-2-(4-methoxyphenylimino) (48%), m.p. 196-198°C (yellow prisms). (Found: C, 59.86; H, 4.23; N, 14.14. $C_{25}H_{21}N_5O_3S_2$ requires: C, 59.64; H, 4.17; N, 13.92); i.r. (Nujol): 3347, 3128, 1687, 1653, 1614, 1541, 1512, 1302, 1252, 1153, 1032, 833, 745, and 690 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+DMSO-d_6): 3.75 (s, 3H, Ar-OCH_3), 3.81 (s, 3H, Ar-OCH_3), 6.82 (d, 2H, J=8.9 Hz), 6.94 (d, 2H, J=9.8 Hz), 7.25 (d, 2H, J=9.8 Hz), 7.49-7.41 (m, 5H), 7.76 (d, 2H, J=8.9 Hz), 9.33 (s, 1H, NH), 9.55 (s, broad, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+DMSO-d_6): 54.76 (OCH_3), 54.97 (OCH_3), 97.09, 113.46, 114.07, 120.61, 126.74, 127.73, 127.91, 128.01, 128.10, 132.48, 132.95, 137.84, 140.30, 154.92, 156.64, 158.15 (C=O), 162.15 (C=S); m/z (%): 503 (M^+, 5), 396 (5), 166 (15), 165 (100), 150 (84), 148 (19), 135 (15), 134 (7), 133 (34), 122 (84), 108 (10), 91 (6), 90 (10), 77 (21).

(3f) 9-(4-Fluorophenylamino)-2-(4-fluorophenylimino) (49%), m.p. 235-237°C (yellow prisms). (Found: C, 57.39; H, 3.08; N, 14.53. $C_{23}H_{15}F_2N_5OS_2$ requires: C, 57.62; H, 3.13; N, 14.61); i.r. (Nujol): 3375, 3273, 1699, 1659, 1619, 1545, 1505, 1325, 1217, 1142, 1092, 847, 833, 741, and 689 cm^{-1}; ^1H n.m.r.

δ (DMSO-d_6): 7.00 (t, 2H, J=8.7 Hz), 7.17 (t, 2H, J=8.5 Hz), 7.33-7.49 (m, 7H), 7.86 (dd, 2H, J_{H-F}=4.6 Hz, J_o=9.1 Hz), 7.93 (s, 1H, NH), 9.59 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 97.97, 114.75 (J=22.1 Hz), 115.69 (J=22.8 Hz), 120.47 (J=7.5 Hz), 127.20 (J=8.6 Hz), 127.93, 128.07, 128.19, 132.01 (J=3.0 Hz), 132.96, 135.59 (J=2.5 Hz), 137.85, 138.71, 156.36 (C=O), 157.62 (J=240.0 Hz), 160.78 (J=247.0 Hz), 162.88 (C=S); m/z (%): 479 (M^+, 5), 326 (5), 154 (15), 153 (100), 136 (30), 135 (20), 119 (5), 110(5), 109 (16), 95 (41), 77 (15).

General Procedure for the Preparation of 2,9-Bis(arylamino)-5-methylthio-7-oxo-6-phenyl imidazo[1,5-*d*][1,3,4]thiadiazin-6-ium Tetrafluoroborates (4).

To a well-stirred suspension of the appropriate imidazo[1,5-*d*][1,3,4]thiadiazine **3** (1 mmol) in dry dichloromethane (5 ml), trimethyloxonium tetrafluoroborate (0.15 g, 1 mmol) was added. The reaction mixture was heated at reflux for 10 h. After cooling, the solution was concentrated to dryness and the residual material was recrystallized from chloroform to give **4**. The following derivatives **4** were obtained:

(4a) 2,9-Bis(4-Tolylamino) (64%), m.p. 142-144°C (yellow prisms). (Found: C, 54.32; H, 4.10; N, 12.38. $C_{28}H_{24}N_5BF_4OS_2$ requires: C, 54.45; H, 4.19; N, 12.22); i.r. (Nujol): 3398, 3296, 1693, 1637, 1612, 1592, 1568, 1514, 1344, 1312, 1213, 1122, 1100, 1068, 1019, 825, 746, and 692 cm^{-1}; ^{1}H n.m r. δ (DMSO-d_6): 2.26 (s, 3H, Ar-CH_3), 2.37 (s, 3H, Ar-CH_3), 2.40 (s, 3H, CH_3S), 7.20 (d, 2H, J=8.4 Hz), 7.30 (d, 2H, J=8.6 Hz), 7.37 (d, 2H, J=8.6 Hz), 7.49-7.65 (m, 8H, ArH+NH), 10.44 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 16.11 (CH_3S), 20.41 (CH_3Ar), 20.64 (CH_3Ar), 96.74, 120.59, 126.26, 128.10, 129.57, 129.62, 129.98, 130.24, 131.51, 133.63, 134.02, 135.67, 138.98, 139.70, 145.03, 149.79, 154.39 (C=O); m/z (%): 486 (M^+-BF_4, 5), 485 (5), 410 (6), 190 (8), 150 (23), 149 (43), 148 (22), 135 (19), 132 (38), 131 (27), 119 (31), 104 (15), 91 (100), 77 (34).

(4b) 2,9-Bis(4-Fluorophenylamino) (83%), m.p. 173-175°C (yellow prisms). (Found: C, 49.69; H, 2.98; N, 12.23. $C_{24}H_{18}BF_6N_5OS_2$ requires: C, 49.58; H, 3.12; N, 12.04); i.r. (Nujol): 3217, 3166, 1695, 1641, 1619, 1569, 1505, 1410, 1227, 1204, 1159, 1097, 1030, 840, 805, 738, and 691 cm^{-1}; ^{1}H n.m.r. δ (DMSO-d_6): 2.39 (s, 3H, CH_3S), 7.25 (t, 2H, J=8.72 Hz), 7.45-7.68 (m, 12H, ArH+NH), 10.75 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 16.15 (CH_3S), 96.94, 115.91 (J=23.1 Hz), 116.67 (J=23.1 Hz), 122.80 (J=8.5 Hz), 128.09, 128.80 (J=9.1 Hz), 129.60, 130.05, 131.45, 132.78 (J=2.5 Hz), 134.43 (J=2.5 Hz), 140.16, 145.23, 149.42, 153.35 (C=O), 158.82 (J=242.5 Hz), 161.83 (J=246.6 Hz); m/z (%): 494 (M^+-BF_4, 5), 493 (8), 207 (10), 154 (10), 153 (100), 137 (17), 136 (21), 135 (39), 126 (11), 119 (10), 109 (21), 95 (50), 94 (11), 91 (6), 77 (21).

General Procedure for the Preparation of 2,9-Bis[Alkyl(aryl)amino]-7-oxo-6-phenyl-5-thioxo-3H-imidazo[1,5-*d*][1,3,4]oxadiazines (5).

These compounds were prepared as described for 3H-imidazo[1,5-*d*][1,3,4]thiadiazines **3**.

(5a) 2,9-Bis(propylamino) (51%), m.p. 201-201°C (white prisms). (Found: C, 56.72; H, 6.12; N, 19.31. $C_{17}H_{21}N_5O_2S$ requires: C, 56.81; H, 5.89; N, 19.48); i.r. (Nujol): 3341, 3177, 1693, 1602, 1552, 1501, 1297, 1257, 1212, 1161, 1070, 1030, 985, 883, 787, 749, 719, and 691 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$+TFA): 0.91 (t, 3H, J=7.4 Hz), 0.94 (t, 3H, J=7.2 Hz), 1.58 (m, 4H), 3.27 (t, 2H, J=7.14 Hz), 3.36 (t, 2H, J=6.7 Hz), 7.40-7.58 (m, 5H), 7.94 (s, 1H, NH), 10.60 (s, broad, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+TFA): 11.13 (CH_3), 11.29 (CH_3), 21.92 (CH_2), 22.88 (CH_2), 41.09 (CH_2), 47.76 (CH_2), 123.75, 129.52, 130.21, 133.01, 156.60, 160.36, 162.49, 163.55, 165.17; m/z (%): 359 (M^+, 5), 192 (10), 136 (15), 135 (30), 119 (10), 91 (6), 85 (13), 84 (32), 77 (24), 56 (100), 55 (97).

(5b) 2,9-Bis(phenylamino) (40%), m.p. 199-201°C (white prisms). (Found: C, 64.39; H, 3.87; N, 16.49. $C_{25}H_{17}N_5O_2S$ requires: C, 64.62; H, 4.01; N, 16.38); i.r. (Nujol): 3370, 3217, 1660, 1649, 1591, 1576, 1547, 1503, 1393, 1309, 1272, 1250, 1177, 1103, 1078, 1045, 939, 916, 902, 891, 748, and 696 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+TFA): 7.05 (t, 1H, J=7.1 Hz), 7.12-7.30 (m, 8H), 7.35-7.52 (m, 6H), 9.26 (s, 1H, NH), 9.73 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+TFA): 120.84, 120.86, 123.92, 124.86, 126.21, 129.13, 129.98, 130.12, 130.40., 132.39, 137.12, 138.14, 156.26, 158.29, 160.82; m/z (%): 427 (M^+, 8), 308 (5), 292 (5), 150 (13), 135 (52), 120 (15), 119 (70), 118 (36), 104 (22), 93 (54), 91 (43), 77 (100).

(5c) 2,9-Bis(4-Tolylamino) (43%), m.p. 208-209°C (white prisms). (Found: C, 66.21; H, 4.92; N, 15.28. $C_{25}H_{21}N_5O_2S$ requires: C, 65.92; H, 4.79; N, 15.37); i.r. (Nujol): 3336, 3160, 1699, 1631, 1597, 1574, 1557, 1319, 1257, 813, 754, and 706 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+TFA): 2.37 (s, 3H, Ar-CH_3), 2.38 (s, 3H, Ar-CH_3), 7.23-7.36 (m, 8H), 7.47-7.53 (m, 2H), 7.61-7.64 (m, 3H), 8.89 (s, 1H, NH), 9.30 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+TFA): 20.66 (CH_3), 20.70 (CH_3), 122.64, 122.94, 123.99, 130.26, 130.98, 131.03, 131.55, 134.56, 138.10, 139.20, 157.99, 164.96; m/z (%): 455 (M^+, 8), 164 (12), 149 (26), 135 (60), 132 (68), 131 (26), 119 (59), 106 (28), 105 (18), 104 (38), 91 (100), 77 (95).

(5d) 2,9-Bis(4-Methoxyphenylamino) (50%), m.p. 195-196°C (white prisms). (Found: C, 61.69; H, 4.12; N, 14.28. $C_{25}H_{21}N_5O_4S$ requires: C, 61.59; H, 4.34; N, 14.36); i.r. (Nujol): 3200, 1665, 1642, 1608, 1580, 1557, 1506, 1302, 1251, 1234, 1172, 1098, 1047, 1030, 928, 838, 804, 747, and 691 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+TFA): 3.79 (s, 3H, CH_3O), 3.81 (s, 3H, CH_3O), 6.89 (d, 2H, J=9.0 Hz), 6.92 (d, 2H, J=9.0 Hz), 7.24 (d, 2H, J=9.0 Hz), 7.39 (d, 2H, J=9.0 Hz), 7.42-7.56 (m, 5H), 8.80 (s, 1H, NH), 9.53 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+TFA): 55.71 (CH_3O), 55.74 (CH_3O), 114.75, 115.73, 123.68, 124.20, 125.30, 129.45, 130.59, 132.31, 156.30, 157.52, 158.61, 159.31, 164.20; m/z (%): 487 (M^+, 6), 380 (4), 150 (25), 149 (95), 148 (18), 135 (49), 134 (64), 133 (18), 123 (15), 122 (10), 119 (100), 108 (28), 104 (8), 91 (42), 77 (26).

(5e) 2,9-Bis(4-Fluorophenylamino) (43%), m.p. 217-219°C (white prisms). (Found: C, 59.39; H, 3.19; N, 15.29. $C_{23}H_{15}F_2N_5O_2S$ requires: C, 59.62; H, 3.26; N, 15.11); i.r. (Nujol): 3336, 1661, 1651, 1645, 1603, 1582, 1539, 1501, 1269, 1223, 1198, 1159, 1113, 1099, 1040, 1028, 910, 833, 814, 770, 748, 721, and 692 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+TFA): 6.94 (t, 2H, J=8.7 Hz), 7.03 (t, 2H, J=8.1 Hz), 7.26 (dd, 2H, J=8.9 Hz, J=4.6 Hz), 7.42-7.59 (m, 7H), 9.19 (s, 1H, NH), 9.72 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+TFA): 116.51 (J=23.1 Hz), 117.51 (J=23.4 Hz), 124.08, 124.75, (J=8.6 Hz), 125.28 (J=8.8 Hz), 130.46 (J=3.0 Hz),131.05, 131.68, 133.16 (J=3.5 Hz), 158.22, 161.51 (J=247.6 Hz), 162.18 (J=245.6 Hz); m/z (%): 463 (M^+, 8), 368 (3), 153 (56), 138 (15), 137 (100), 136 (46), 135 (27), 119 (15), 110 (17), 109 (86), 95 (37), 91 (12), 77 (28).

Preparation of 3-Substituted 5-alkylamino-2-phenylimino[1,3,4]thiadiazoles (6).

To a mixture of iminophosphorane **2** (0.93 g, 2 mmol) in dry methanol (10 ml), the appropriate alkyl isocyanate (4 mmol) was added. The reaction mixture was stirred at room temperature until the solid was dissolved. Then, the solution was concentrated to dryness and the residual material was washed with cold dichloromethane/hexane (1:1) (3x10 ml). The resulting solid was recrystallized from acetonitrile to give **6**. The following derivatives **6** were obtained:

(6a) 5-Ethylamino (56%), m.p. 160-161°C (white prisms). (Found: C, 53.61; H, 5.38; N, 18.79. $C_{13}H_{16}N_4O_2S$ requires: C, 53.42; H, 5.48; N, 19.18); i.r. (Nujol): 3330, 1750, 1631, 1597, 1518, 1381, 1217, 968, 860, 776, 725, and 702 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 1.95 (t, 3H, J=7.2 Hz, CH_3-), 3.23 (dq, 2H, J=7.2

Hz, J=5.6 Hz, -CH_2-NH), 3.77 (s, 3H, CH_3O), 4.10 (s, broad, 1H, NH), 4.68 (s, 2H, CH_2-$COOCH_3$), 6.95-7.07 (m, 3H), 7.20-7.35 (m, 2H); ^{13}C n.m.r. δ ($CDCl_3$): 14.82 (CH_3), 39.54 (CH_2), 49.24 (*C*H_2-COO-), 52.10 (*C*H_3OOC-), 121.15, 123.27, 129.34, 148.99, 152.03, 155.35, 168.74; m/z (%): 292 (M^+, 5), 233 (10), 135 (25), 98 (100), 88 (20), 77 (51), 60 (23), 59 (18), 45 (25), 43 (98).

(6b) 5-t-Butylamino (47%), oil. (Found: C, 56.01; H, 6.46; N, 17.25. $C_{15}H_{20}N_4O_2S$ requires: C, 56.25; H, 6.25; N, 17.50); i.r. (Nujol): 3375, 1755, 1636, 1568, 1393, 1365, 1263, 1217, 1025, 985, 866, 798, 770, and 690 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 1.33 (s, 9H, $(CH_3)_3C$), 3.77 (s, 3H, CH_3OOC-), 4.00 (s, broad, 1H, NH), 4.69 (s, 2H, CH_2-$COOCH_3$), 6.96-7.06 (m, 3H), 7.26-7.33 (m, 2H); ^{13}C n.m.r. δ ($CDCl_3$): 29.03 (CH_3), 49.03 (CH_2), 52.09 (*C*H_3OOC), 53.24, 121.03, 123.12, 129.23, 146.61, 151.87, 155.44, 168.67; m/z (%): 320 (M^+, 10), 264 (10), 205 (38), 136 (30), 135 (45), 104 (8), 77 (44), 70 (100), 57 (77).

General Procedure for the Preparation of 1-Substituted 4-Aryl-3-arylamino-5-thioxo-4,5-dihydro[1,2,4]triazoles (7).

To a solution of 1-amino-3-phenyl-2-thioxo-4-imidazolidinone **1** (1.03 g, 5 mmol) in dry toluene (30 ml), a solution of the appropriate diarylcarbodiimide (5 mmol) in the same solvent (15 ml) was added. The reaction mixture was stirred at reflux temperature for 24 h. After cooling, the precipitated solid was collected by filtration, washed with cold methanol (2x10 ml), air-dried and recrystallized from methanol to give **7**. The following derivatives **7** were obtained:

(7a) 4-Phenyl-3-phenylamino (42%), m.p. 228-230°C (colourless prisms). (Found: C, 65.68; H, 4.86; N, 17.34. $C_{22}H_{19}N_5OS$ requires: C, 65.82; H, 4.77; N, 17.44); i.r. (Nujol): 3251, 3194, 3137, 1688, 1622, 1606, 1593, 1555, 1334, 1253, 1240, 1232, 1201, 1043, 1024, 952, 853, 759, 749, and 691 cm^{-1}; ^{1}H n.m.r. δ (DMSO-d_6): 5.04 (s, 2H, CH_2-CONH), 6.93 (t, 1H, J=7.3 Hz), 7.07 (t, 1H, J=7.5 Hz), 7.25 (t, 2H, J=7.4 Hz), 7.33 (t, 2H, J=7.5 Hz), 7.44-7.73 (m, 9H), 8.58 (s, 1H, NH), 10.30 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 51.32 (*C*H_2-CO-), 118.07, 119.27, 121.64, 123.51, 128.54, 128.70, 129.41, 129.51, 133.09, 138.45, 139.72, 147.19 (C-3), 164.16 (C=S), 166.06 (C=O); m/z (%): 401 (M^+, 31), 309 (12), 282 (14), 281 (22), 146 (39), 136 (19), 135 (16), 131 (11), 119 (22), 118 (100), 93 (11), 92 (17), 91 (14), 77 (63).

(7b) 4-(4-Tolyl)-3-(4-tolylamino) (51%), m.p. 232-234°C (colourless prisms). (Found: C, 67.03; H, 5.62; N, 16.48. $C_{24}H_{23}N_5OS$ requires: C, 67.11; H, 5.40; N, 16.30). i.r. (Nujol): 3245, 3200, 3137, 1687, 1614, 1552, 1516, 1333, 1312, 1238, 1200, 1036, 955, 922, 856, 816, 759, and 708 cm^{-1}; ^{1}H n.m.r. δ (DMSO-d_6): 2.21 (s, 3H, CH_3Ar), 2.40 (s, 3H, CH_3Ar), 5.01 (s, 2H, CH_2-CONH), 7.05 (d, 2H, J=8.4 Hz), 7.21-7.45 (m, 9H), 7.61 (d, 2H, J=7.9 Hz), 8.38 (s, 1H, NH), 10.29 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 20.20 (CH_3), 20.77 (CH_3), 51.31 (CH_2), 118.37, 119.28, 123.51, 128.49, 128.70, 128.93, 129.98, 130, 49, 130.60, 137.11, 138.48, 139.12, 147.56 (C-3), 164.22 (C=S), 166.01 (C=O); m/z (%): 429 (M^+, 20), 337 (10), 309 (25), 160 (26), 150 (12), 149 (13), 133 (15), 132 (100), 119 (5), 106 (13), 92 (9), 91 (38), 77 (18).

(7c) 4-(4-Methoxyphenyl)-3-(4-methoxyphenylamino) (45%), m.p. 202-204°C (colourless prisms). (Found: C, 62.33; H, 4.85; N, 15.37. $C_{24}H_{23}N_5O_3S$ requires: C, 62.46; H, 5.02; N, 15.17); i.r. (Nujol): 3251, 3200, 3137, 3086, 1684, 1620, 1553, 1516, 1333, 1254, 1229, 1185, 1037, 955, 832, 772, 760, and 713 cm^{-1}; ^{1}H n.m.r. δ (DMSO-d_6): 3.68 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 4.99 (s, 2H, CH_2-CONH), 6.84 (d, 2H, J=9.0 Hz), 7.07 (t, 1H, J=7.6 Hz), 7.12 (d, 2H, J=8.9 Hz), 7.33 (t, 2H, J=7.8 Hz), 7.36 (d, 2H, J=8.9z), 7.42 (d, 2H, J=9.0 Hz), 7.61 (d, 2H, J=7.8 Hz), 8.25 (s, 1H, NH), 10.24 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 51.32 (CH_2), 55.14 (CH_3O), 55.42 (CH_3O), 113.84, 114.76, 119.30, 120.32, 123.58, 125.61, 128.78, 130.16, 132.64, 138.53, 148.51 (C-3), 154.50, 159.89, 164.34 (C=S), 166.06 (C=O);

m/z (%): 461 (M^+, 10), 342 (11), 341 (15), 327 (10), 165 (180), 148 (100), 147 (14), 134 (8), 133 (34), 122 (14), 77 (13).

(7d) 4-(4-Fluorophenyl)-3-(4-fluorophenylamino) (55%), m.p. 268-270°C (yellow prisms). (Found: C, 60.21; H, 4.13; N, 15.92. $C_{22}H_{17}F_2N_5OS$ requires: C, 60.40; H, 3.92; N, 16.01); i.r. (Nujol): 3251, 3200, 3143, 3086, 1685, 1622, 1602, 1555, 1509, 1336, 1239, 1227, 1213, 1165, 1035, 952, 899, 862, 846, 788, 756, and 710 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 5.03 (s, 2H, CH_2-CONH), 7.07 (t, 1H, J=7.5 Hz), 7.11 (t, 2H, J=8.7 Hz), 7.33 (t, 2H, J=7.7 Hz), 7.50-7.75 (m, 8H), 8.57 (s, broad, 1H, NH), 10.24 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 51.38 (CH_2), 115.14 (J=23.4 Hz), 116.48 (J=23.2 Hz), 119.36, 120.07 (J=8.0 Hz), 123.59, 128.73, 129.30 (J=3 Hz), 131.34 (J=9.3 Hz), 135.86 (J=2.4 Hz), 138.45, 147.49 (C-3), 157.33 (J=238.6 Hz), 162.45 (J=246.5 Hz), 164.18 (C=S), 166.11 (C=O); m/z (%): 437 (M^+, 16), 345 (10), 318 (14), 317 (20), 164 (28), 154 (13), 153 (14), 136 (100), 135 (18), 110 (14), 109 (12), 95 (25), 91 (15), 77 (18).

(7e) 4-(4-Chlorophenyl)-3-(4-chlorophenylamino) (50%), m.p. 287-289°C (colourless prisms). (Found: C, 55.93; H, 3.51; N, 15.07. $C_{22}H_{17}Cl_2N_5OS$ requires: C, 56.18; H, 3.64; N, 14.89); i.r. (Nujol): 3239, 3188, 3126, 3075, 1682, 1619, 1605, 1592, 1554, 1314, 1239, 1093, 1035, 1018, 957, 899, 855, 829, 755, 740, and 708 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 5.04 (s, 2H, CH_2-CONH), 7.07 (t, 1H, J=7.0 Hz), 7.20-7.69 (m, 12H), 8.79 (s, 1H, NH), 10.28 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 51.39 (CH_2), 119.35, 119.62, 123.57, 125.43, 128.41, 128.71, 129.61, 130.82, 131.83, 134.42, 138.41, 138.50, 146.82 (C-3), 164.10 (C=S), 166.00 (C=O); m/z (%): 471 (M^++2, 4), 469 (M^+, 5), 379 (4), 377 (5), 352 (6), 351 (10), 350 (9), 349 (13), 182 (10), 180 (31), 154 (32), 152 (100), 128 (6), 126 (17), 113 (9), 111 (30), 92 (43), 91 (60), 77 (26).

(7f) 4-(4-Bromophenyl)-3-(4-bromophenylamino) (50%), m.p. 263-265°C (yellow prisms). (Found: C, 47.13; H, 2.83; N, 12.72. $C2_2H_{17}Br_2N_5OS$ requires: C, 47.25; H, 3.06; N, 12.52); i.r. (Nujol): 3239, 3075, 1682, 1616, 1607, 1588, 1550, 1238, 1074, 1036, 1014, 957, 853, 825, 755, 724, and 705 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 5.02 (s, 2H, CH_2-CONH), 7.04-7.50 (m, 9H), 7.60 (d, 2H, J=7.8 Hz), 7.80 (d, 2H, J=8.4 Hz), 8.79 (s, 1H, NH), 10.26 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 51.39 (CH_2), 113.27, 119.35, 120.02, 123.08, 123.57, 128.72, 131.09, 131.35, 132.27, 132.57, 138.41, 138.94, 146.70 (C-3), 164.05 (C=S), 165.94 (C=O); m/z (%): 559 (M^++2, 2), 441 (2), 439 (4), 226 (9), 224 (9), 215 (17), 213 (14), 198 (99), 196 (100), 173 (12), 172 (11), 171 (12), 170 (11), 157 (31), 155 (32), 135 (25), 134 (16), 92 (25), 91 (26), 77 (49).

General Procedure for the Preparation of 1-Substituted 4-Aryl-3-arylamino-5-methylthio-[1,2,4]triazol-4-ium Tetrafluoroborates (8).

To a well-stirred solution of the appropriated 4,5-dihydro[1,2,4]triazole **7** (3 mmol) in dry dichloromethane (20 ml), trimethyloxonium tetrafluoroborate (0.44 g, 3mmol) was added. The reaction mixture was stirred at reflux temperature for 10 h. After cooling, the precipitated solid was collected by filtration and recrystallized from methanol to give **8**. The following derivatives **8** were obtained:

(8a) 4-Phenyl-3-phenylamino (66%), m.p. 216-218°C (white prisms). (Found: C, 55.06; H, 4.37; N, 14.06. $C_{23}H_{22}BF_4N_5OS$ requires: C, 54.89; H, 4.41; N, 13.91); i.r. (Nujol): 3302, 3149, 1687, 1625, 1604, 1588, 1553, 1319, 1260, 1118, 1081, 965, 850, 764, 756, and 721 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 2.27 (s, 3H), 5.42 (s, 2H, CH_2-CONH), 7.03-7.15 (m, 2H), 7.31-7.41 (m, 4H), 7.50 (s, 2H, J=7.9 Hz), 7.60 (d, 2H, J=7.8 Hz), 7.76 (s, 5H), 9.47 (s, 1H, NH), 10.63 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 17.24 (CH_3), 54.17 (CH_2), 119.43, 119.71, 123.69, 124.27, 128.38, 128.94, 129.03, 130.16, 130.48, 131.84, 137.93, 137.99,

148.97 (C-3), 151.63 (C-5), 162.28 (C=O); m/z (%): 416 (M^+-BF_4, 2), 401 (10), 282 (10), 281 (15), 146 (28), 136 (12), 135 (13), 132 (10), 131 (12), 120 (5), 119 (35), 118 (100), 117 (11), 104 (13), 92 (22), 91 (41), 77 (75).

(8b) 4-(4-Tolyl)-3-(4-tolylamino) (70%), m.p. 105-107°C (colourless prisms). (Found: C, 56.32; H, 5.19; N, 13.33. $C_{25}H_{26}BF_4N_5OS$ requires: C, 56.51; H, 4.93; N, 13.18); i.r. (Nujol): 3113, 1694, 1625, 1612, 1508, 1380, 1318, 1234, 1058, 818, 758, and 721 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 2.24 (s, 3H, CH_3S), 2.29 (s, 3H, Ar-CH_3), 2.47 (s, 3H, Ar-CH_3), 5.41 (s, 2H), 7.14 (d, 2H, J=8.1 Hz), 7.33-7.78 (m, 11H), 9.36 (s, 1H, NH), 10.66 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 17.25 (CH_3S), 20.31 (Ar-CH_3), 20.91 (Ar-CH_3), 54.14 (CH_2), 119.48, 120.03, 124.27, 128.10, 129.00, 129.31, 130.93, 132.92, 135.37, 137.93, 138.69, 141.82, 148.80 (C-3), 151.95 (C-5), 162.31 (C=O); m/z (%): 444 (M^+-BF_4, 5), 443 (10), 430 (21), 429 (75), 311 (20), 310 (88), 309 (82), 277 (6), 160 (15), 149 (15), 132 (100), 131 (41), 107 (22), 106 (28), 92 (13), 91 (67), 77 (37).

(8c) 4-(4-Methoxyphenyl)-3-(4-methoxyphenylamino) (77%), m.p. 105-107°C (white prisms). (Found: C, 53.04; H, 4.79; N, 12.33. $C_{25}H_{26}BF_4N_5O_3S$ requires: C, 53.30; H, 4.65; N, 12.43); i.r. (Nujol): 3341, 3217, 1690, 1630, 1597, 1562, 1512, 1308, 1250, 1182, 1082, 1024, 956, 828, 758, 743, and 692 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$+DMSO-d_6): 2.31 (s, 3H, CH_3S), 3.73 (s, 3H, CH_3O), 3.90 (s, 3H, CH_3O), 5.76 (s, 2H), 6.88 (d, 2H, J=9.0 Hz), 7.08 (t, 1H, J=7.8 Hz), 7.23 (d, 2H, J=8.8 Hz), 7.32 (t, 2H, J=8.0 Hz), 7.38 (d, 2H, J=9.0 Hz), 7.59 (d, 2H, J=8.0 Hz), 7.68 (d, 2H, J=8.8 Hz), 9.21 (s, 1H, NH), 10.59 (s, 1H, NH); ^{13}C n.m.r. δ ($CDCl_3$+DMSO-d_6): 17.04 (CH_3S), 53.99 (CH_2), 55.06 (CH_3O), 55.57 (CH_3O), 113.91, 115.45, 119.35, 121.95, 122.20, 124.07, 128.76, 129.67, 130.56, 137.83, 148.61 (C-3), 152.44 (C-5), 155.80, 161.36, 162.07 (C=O); m/z (%): 476 (M^+-BF_4, 5), 461 (26), 369 (12), 368 (10), 342 (40), 341 (38), 327 (24), 148 (89), 147 (29), 134 (50), 133 (73), 122 (43), 121 (45), 120 (42), 119 (51), 107 (23), 106 (40), 93 (37), 92 (26), 91 (33), 77 (81).

(8d) 4-(4-Fluorophenyl)-3-(4-fluorophenylamino) (80%), m.p. 216-218°C (yellow prisms). (Found: C, 50.97; H, 3.85; N, 13.17. $C_{23}H_{20}BF_6N_5OS$ requires: C, 51.22; H, 3.74; N, 12.98); i.r. (Nujol): 3358, 1701, 1627, 1600, 1558, 1541, 1510, 1316, 1297, 1244, 1230, 1101, 1056, 1018, 848, 839, 817, 789, 760, 726, and 707 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 2.33 (s, 3H), 5.43 (s, 2H), 7.12 (t, 1H, J=7.2 Hz), 7.21 (d, 2H, J= 9.0 Hz), 7.37 (t, 2H, J=7.9 Hz), 7.50-7.66 (m, 6H), 7.92 (dd, 2H, J=9.0 Hz, J=4.8 Hz), 9.49 (s, 1H, NH), 10.67 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 17.33 (CH_3S), 54.19 (CH_2), 115.63 (J=22.6 Hz), 117.58 (J=23.4 Hz), 119.47, 121.93 (J=8.0 Hz), 124.28, 126.32 (J=3.0 Hz), 129.00, 131.21 (J=9.8 Hz), 134.19 (J=2.6 Hz), 137.93, 149.03 (C-3), 151.94 (C-5), 158.46 (J=240.8 Hz), 162.19 (C=O), 163.71 (J=249.5 Hz); m/z (%): 451 (M^+-BF_4, 2), 437 (5), 345 (2), 318 (16), 317 (8), 164 (11), 150 (9), 149 (9), 136 (100), 135 (13), 110 (13), 109 (30), 95 (20), 77 (13).

(8e) 4-(4-Chlorophenyl)-3-(4-chlorophenylamino) (89%), m.p. 219-221°C (white prisms). (Found: C, 48.18; H, 3.69; N, 12.46. $C_{23}H_{20}BCl_2F_4N_5OS$ requires: C, 48.28; H, 3.52; N, 12.24); i.r. (Nujol): 3341, 3234, 1704, 1623, 1602, 1587, 1549, 1313, 1093, 1058, 1019, 837, 825, and 760 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 2.33 (s, 3H), 5.44 (s, 2H), 7.12 (t, 1H, J=7.4 Hz), 7.37 (t, 2H, J=7.6 Hz), 7.42 (d, 2H, J=9.0 Hz), 7.53 (d, 2H, J=9.0 Hz), 7.61 (d, 2H, J=7.9 Hz), 7.85 (s, 4H), 9.62 (s, 1H, NH), 10.68 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 17.45 (CH_3S), 54.19 (CH_2), 119.39, 121.02, 124.26, 127.41, 128.88, 129.02, 130.50, 130.62, 136.78, 136.88, 137.91, 149.13 (C-3), 151.27 (C-5), 162.11 (C=O); m/z (%): 486 (M^++2-BF_4, 2), 484 (M^+-BF_4, 3), 483 (12), 471 (3), 469 (5), 366 (2), 364 (3), 182 (4), 180 (13), 154 (32), 152 (100), 128 (7), 127 (32), 126 (18), 125 (41), 113 (14), 111 (35), 92 (17), 91 (22), 77 (49).

General Procedure for the Preparation of 1-Substituted 4-Aryl-3-arylamino-5-oxo-4,5-dihydro[1,2,4]triazoles (9).

To a solution of the appropriate 1,2,4-triazol-4-ium tetrafluoroborate **8** (1 mmol) in methanol (20 ml), triethylamine (0.30 g, 3 mmol) was added. The reaction mixture was stirred at room temperature for 7 h. The separated solid was collected by filtration and recrystallized from methanol to give **9**. The following derivatives **9** were obtained:

(9a) 4-Phenyl-3-phenylamino (77%), m.p. 266-268°C (colourless needles). (Found: C, 68.43; H, 5.19; N, 18.33. $C_{22}H_{19}N_5O_2$ requires: C, 68.56; H, 4.97; N, 18.17); i.r. (Nujol): 3268, 3251, 3143, 1716, 1700, 1682, 1605, 1557, 1500, 1257, 1124, 1062, 954, 852, 751, and 692 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 4.56 (s, 2H), 6.85 (t, 1H, J=7.3 Hz), 7.05 (t, 1H, J=7.4 Hz), 7.19 (t, 2H, J=7.3 Hz), 7.27-7.54 (m, 9H), 7.60 (d, 2H, J=7.5 Hz), 8.39 (s, 1H, NH), 10.21 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 48.15 (CH_2), 117.56, 119.40, 121.06, 123.64, 127.47, 128.60, 128.68, 128.86, 129.48, 132.33, 138.64, 140.54, 142.69 (C-3), 152.26 (C=O), 165.58 (C=O); m/z (%): 385 (M^+, 16), 265 (29), 146 (46), 120 (12), 119 (37), 118 (100), 93 (10), 92 (18), 91 (15), 77 (40).

(9b) 4-(4-Tolyl)-3-(4-tolylamino) (77%), m.p. 221-223°C (colourless needles). (Found: C, 69.65; H, 5.73; N, 17.17. $C_{24}H_{23}N_5O_2$ requires: C, 69.72; H, 5.61; N, 16.94); i.r. (Nujol): 3432, 3256, 3200, 1725, 1693, 1604, 1548, 1514, 1316, 1127, 1074, 955, 813, 742, and 692 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 2.18 (s, 3H), 2.37 (s, 3H), 4.52 (s, 2H), 6.99 (d, 2H, J=8.5 Hz), 7.06 (t, 1H, J=7.3 Hz), 7.20-7.37 (m, 8H), 7.58 (d, 2H, J=7.8 Hz), 8.13 (s, 1H, NH), 10.16 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 20.33 (Ar-CH_3), 20.72 (Ar-CH_3), 48.15 (CH_2), 117.76, 119.31, 123.54, 127.37, 128.77, 128.95, 129.57, 129.80, 129.91, 137.81, 138.16, 138.56, 143.01 (C-3), 152.25 (C=O), 165.55 (C=O); m/z (%): 413 (M^+, 10), 293 (20), 161 (3), 160 (21), 134 (5), 133 (21), 132 (100), 131 (24), 106 (13), 105 (5), 92 (6), 91 (17), 77 (17).

(9c) 4-(4-Methoxyphenyl)-3-(4-methoxyphenylamino) (75%), m.p. 221-223°C (colourless needles). (Found: C, 64.63; H, 5.10; N, 15.67. $C_{24}H_{23}N_5O_4$ requires: C, 64.71; H, 5.20; N, 15.72); i.r. (Nujol): 3421, 3290, 3137, 1722, 1699, 1611, 1559, 1513, 1304, 1257, 1237, 1043, 953, 826, 783, 744, and 690 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 3.66 (s, 3H), 3.81 (s, 3H), 4.51 (s, 2H), 6.80 (d, 2H, J=8.9 Hz), 7.07-7.11 (m, 3H), 7.39-7.60 (m, 6H), 7.60 (d, 2H, J=7.9 Hz), 8.01 (s, 1H, NH), 10.16 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 48.16 (CH_2), 55.13 (CH_3O), 55.44 (CH_3O), 113.83, 114.71, 119.33, 119.66, 123.56, 124.65, 128.79, 129.23, 133.30, 138.49, 143.70 (C-3), 152.45 (C=O), 154.02, 159.36, 165.65 (C=O); m/z (%): 445 (M^+, 5), 325 (16), 177 (2), 176 (7), 149 (27), 148 (100), 147 (11), 133 (23), 122 (10), 120 (5), 107 (3), 92 (6), 77 (10).

(9d) 4-(4-Fluorophenyl)-3-(4-fluorophenylamino) (67%), m.p. 244-246°C (colourless prisms). (Found: C, 62.51; H, 3.92; N, 16.39. $C_{22}H_{17}F_2N_5O_2$ requires: C, 62.70; H, 4.07; N, 16.62); i.r. (Nujol): 3256, 3117, 3092, 1705, 1679, 1619, 1603, 1555, 1314, 1257, 1212, 1031, 902, 833, 794, 754, 735, 709, and 694 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 4.55 (s, 2H), 7.00-7.10 (m, 3H), 7.32 (t, 2H, J=7.9 Hz), 7.39-7.54 (m, 6H), 7.60 (d, 2H, J=7.9 Hz), 8.39 (s, 1H, NH), 10.17 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 48.19 (CH_2), 115.11 (J=22.3 Hz), 116.38 (J=23.0 Hz), 119.34, 119.45, 123.57, 128.35 (J=3.0 Hz), 128.78, 130.07 (J=9.0 Hz), 136.50 (J=2.5 Hz), 138.54, 142.91 (C-3), 152.13 (C=O), 156.93 (J=238.0 Hz), 161.88 (J=245.5 Hz), 165.48 (C=O); m/z (%): 421 (M^+, 11), 301 (16), 164 (35), 137 (37), 136 (100), 135 (17), 120 (4), 110 (17), 109 (15), 95 (11), 92 (6), 77 (13).

(9e) 4-(4-Chlorophenyl)-3-(4-chlorophenylamino) (92%), m.p. 245-247°C (colourless needles). (Found: C, 57.93; H, 3.66; N, 14.27. $C_{22}H_{17}Cl_2N_5O_2$ requires: C, 58.16; H, 3.77; N, 15.41); i.r. (Nujol): 3245, 3283, 3126, 1705, 1698, 1682, 1623, 1606, 1557, 1325, 1250, 1095, 900, 827, 771, 755, and 708 cm^{-1}; ^1H n.m.r. δ (DMSO-d_6): 4.57 (s, 2H), 7.06 (t, 1H, J=7.3 Hz), 7.24-7.35 (m, 4H), 7.40-7.53 (m, 4H), 7.60 (t, 4H, J=8.6 Hz), 8.62 (s, 1H, NH), 10.20 (s, 1H, NH); ^{13}C n.m.r. δ (DMSO-d_6): 48.18 (CH_2), 119.03, 119.32, 123.56, 124.66, 128.43, 128.74, 129.39, 129.49, 130.89, 133.30, 138.47, 139.14, 142.18 (C-3), 151.85 (C=O), 165.35 (C=O); m/z (%): 445 (M^++2, 3), 453 (M^+, 4), 337 (2), 335 (10), 333 (18), 155 (9), 154 (31), 153 (32), 152 (100), 128 (5), 126 (15), 113 (5), 111 (14), 92 (9), 77 (22).

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