Pergamon

Tetrahedron, Vol. 53, No. 6, pp. 2125-2136, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(96)01108-8

Reactions of Arylazosulfones with the Conjugate Bases of (*tert*-Butoxycarbonyl)methyl and Tosylmethyl Isocyanide. Synthesis of Substituted 1-Arylimidazoles

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Abstract: The reactions of arylazosulfones **1** ($ArN{=}NSO_2Ar'$) with the potassium salts of (*tert*-butoxycarbonyl)methyl **2** and tosylmethyl isocyanide **3** in DMSO afford 4,5-bis(*tert*-butoxycarbonyl)- **4** and 4-tosyl-1-arylimidazoles **5**, respectively. Yields of imidazoles **4** and **5** vary from moderate to excellent depending on the nature both of Ar in **1** and of the nucleophile (**2** or **3**) employed. A comparison of the results obtained with those relevant to the reactions of the same nucleophiles with nitrosobenzene in analogous experimental conditions provides useful mechanistic indications on the transformation of **1** to **4** or **5**.

The behaviour of covalent adducts of arenediazonium salts (Ar-N=N-X) toward anionic nucleophiles has been the subject of an extensive study in our research group over a long period. In particular, we have shown that arylazosulfides (ArN=NSR) are easily accessible, versatile compounds whose reactivity has proved to be sometimes unpredictable. For instance, azosulfides are effective arylating agents of a number of different carbon nucleophiles[1] *via* $S_{RN}1$ processes;[2] on the other hand, when opportunely substituted in the aryl moiety, they can act as arylhydrazonylating agents toward enolates of ketones,[3] esters and amides,[4] or give a base-induced cyclization to indazole derivatives.[5]

More recently we turned our attention to the behaviour with nucleophiles of another class of covalent adducts of arenediazonium salts, namely the arylazosulfones ($ArN{=}NSO_2Ar'$, **1**) and the somehow unexpected results obtained so far are encouraging as regards possible novel synthetic applications. For example, while arylazosulfides act as $S_{RN}1$ arylating agents toward the conjugate bases of active-methylene compounds (^-CHXY),[1d,6] arylazosulfones accomplish an overall oxidative coupling of such nucleophiles to furnish tetrasubstituted ethylenes.[7] As an extension of the latter studies, we have investigated the reactivity of arylazosulfones with the conjugate bases of two typical active-methylene isonitriles, *i.e.* *tert*-butyl isocyanoacetate (TBICA) and tosylmethyl isocyanide (TosMIC), and the results obtained are herein reported.

RESULTS AND DISCUSSION

Reactions of arylazosulfones with TBICA and TosMIC in DMSO/Bu^{t}OK

Arylazo *p*-tolyl sulfones **1a-k** react with the potassium salts of TBICA (**2**) and TosMIC (**3**) in DMSO to give (Scheme 1) imidazoles **4** and **5**, respectively, in generally good yields (Tables 1 and 2).

Scheme 1

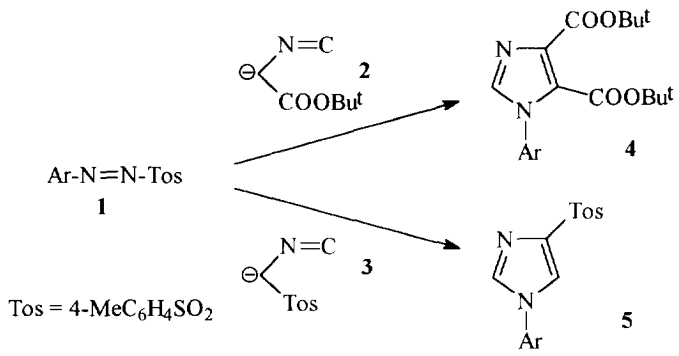


Table 1. 1-Aryl-4,5-bis(*tert*-butoxycarbonyl)imidazoles **4** from azosulfones Ar-N=N-Tos **1a-k** and the potassium salt of TBICA (**2**) in DMSO.[a]

Entry	1	Ar	4	Yield (%) [b]
1	**1a**	C_6H_5	**4a**	82
2	**1b**	4-MeC_6H_4	**4b**	75
3	**1b**	4-MeC_6H_4	**4b**	68 [c]
4	**1c**	3-$MeOC_6H_4$	**4c**	86
5	**1d**	4-$MeOC_6H_4$	**4d**	65
6	**1e**	2-ClC_6H_4	**4e**	62
7	**1f**	3-ClC_6H_4	**4f**	87
8	**1g**	4-ClC_6H_4	**4g**	85
9	**1h**	4-BrC_6H_4	**4h**	65
10	**1i**	2-$NO_2C_6H_4$	**4i**	23 [d,e]
11	**1j**	4-$NO_2C_6H_4$	**4j**	28 [d,f]
12	**1k**	2-naphthyl	**4k**	89

a) [Azosulfone] = 0.067 M; [TBICA] = [Bu^{t}OK] = 0.20 M, unless otherwise indicated. *b*) Yields are based on azosulfone and refer to isolated products; the coproduct $TosNH_2$ was always present in consistent yield. *c*) [Azosulfone] = 0.067 M; [TBICA] = [Bu^{t}OK] = 0.134 M. *d*) The reaction gives a complex mixture. *e*) Several by-products, accounting for an overall 75% material balance, were isolated and identified (see text). *f*) No attempt was made to isolate and characterize by-products.

In agreement with microanalytical data, assignment of structure **4** was essentially based on spectroscopic (^{1}H-, ^{13}C-NMR and IR) results. Furthermore, for a definitive confirmation, the imidazole **4b** was hydrolized to the corresponding dicarboxylic acid. By reaction with aniline, the latter was then transformed, *via* a condensation/decarboxylation process analogous to that reported for 1-methyl-4,5-dicarboxyimidazole[8] into a compound which gave ^{1}H- and ^{13}C-NMR data consistent with the expected 1-(4-methylphenyl)-4-(phenylcarbamoyl)imidazole structure: in particular, H-2 and H-5 of the heterocycle appeared as doublets with a coupling constant ($J_{2,5}$ 1.4 Hz) well within the range (1.1÷1.5 Hz) expected for 1,4-disubstituted imidazoles.[9] Assignment of structure **5** in turn rested on spectroscopic and microanalytical data. In particular,

in the ^{1}H-NMR spectra of compounds **5** H-2 and H-5 always appeared as doublets with a $J_{2,5}$ of 1.2÷1.5 Hz, again in agreement with the just mentioned values expected for 1,4-disubstituted imidazoles; in the off-resonance ^{13}C-NMR of **5j** moreover, the measured three-bond carbon-hydrogen coupling constants ($^3J_{CH}$ 7.2 and 3.1 Hz) are consistent respectively with a C2/H5 and C5/H2 coupling in the imidazole ring.[10]

From a synthetic point of view, the easy access to 4,5-bis(*tert*-butoxycarbonyl)- **4** and 4-tosyl-1-arylimidazoles **5** *via* the studied reactions is of interest given the importance of imidazole derivatives as potential biologically-active agents.[11]

As far as the reactions with the nucleophile **2** are concerned, results reported in Table 1 show a generally high efficiency of the process leading to **4**, with the exception of entries 10 and 11 for (nitrophenyl)azosulfones. In the latter experiments, the formation of imidazoles **4i** and **4j** is accompanied by a number of by-products. Thus, the complex mixture resulting from the reaction of the 2-nitro derivative **1i** with **2** was exhaustively analyzed with identification of the following compounds, which together with **4i** account for a 75% material balance: 1-(2-nitrophenyl)-2-tosylhydrazine (16%), 2-nitroaniline (10%), 2-nitrophenylurea (10%) and 2-nitrophenylcyanamide (16%). In the case of the reaction with **1j** analogous compounds were detected (TLC, ^{1}H-NMR) but not fully characterized or quantified. The nature of the by-products identified suggests the occurrence of a number of pathways in competition with the formation of imidazoles, among which a redox process could be favoured by the presence of a strongly electron-

Table 2. 1-Aryl-4-tosylimidazoles **5** from azosulfones Ar-N=N-Tos **1a-k**, **1'b**[a] and **1'g**[b] and the potassium salt of TosMIC (**3**) in DMSO.[c]

Entry	1	Ar	5	Yield (%) [d]
13	**1a**	C_6H_5	**5a**	60
14	**1b**	4-MeC_6H_4	**5b**	62
15	**1'b**	4-MeC_6H_4	**5b**	66
16	**1b**	4-MeC_6H_4	**5b**	61 [e]
17	**1c**	3-$MeOC_6H_4$	**5c**	77
18	**1d**	4-$MeOC_6H_4$	**5d**	33
19	**1e**	2-ClC_6H_4	**5e**	51
20	**1f**	3-ClC_6H_4	**5f**	74
21	**1g**	4-ClC_6H_4	**5g**	80
22	**1'g**	4-ClC_6H_4	**5g**	70 [e]
23	**1'g**	4-ClC_6H_4	**5g**	69 [f]
24	**1h**	4-BrC_6H_4	**5h**	72
25	**1i**	2-$NO_2C_6H_4$	**5i**	- [g]
26	**1j**	4-$NO_2C_6H_4$	**5j**	50
27	**1k**	2-naphthyl	**5k**	45

a) (4-Methylphenyl)azo phenyl sulfone. *b*) (4-Chlorophenyl)azo phenyl sulfone. *c*) [Azosulfone] = 0.067 M; [TosMIC] = [Bu^{t}OK] = 0.20 M, unless otherwise indicated. *d*) Yields are based on azosulfone and refer to isolated products. *e*) [Azosulfone] = 0.067M; [TosMIC] = [Bu^{t}OK] = 0.134 M. *f*) In DMF. *g*) The reaction gives a very complex mixture in which imidazole **5i** was not observed.

withdrawing nitro group on the aryl moiety of the arylazosulfone.

Throughout the reactions of Table 1, *p*-toluenesulfonamide was always isolated as a coproduct in yields consistent with those of **4**. This, together with the ascertained (entry 3) stoichiometry of the process (eq. 1), suggests that the mechanism involved in the formation of **4** from **1** (which will be discussed later) could bear some analogies with that previously advanced[7] for the reactions of the same azosulfones **1** with the conjugate bases of malononitrile, ethyl cyanoacetate and diethyl malonate.

$$\underset{}{\text{Ar-N=N-Tos}} + \underset{\mathbf{2}}{2\,^{\ominus}\text{CH(NC)(COOBu}^{t})} \longrightarrow \mathbf{4} + \text{TosNH}^{\ominus} + \text{CN}^{\ominus} \qquad \text{(eq. 1)}$$

As concerns the analogous reactions of **1** with nucleophile **3**, the results obtained (Table 2) show overall satisfactory yields of 1,4-disubstituted imidazoles **5**, with the exceptions of entries 18 and 25. The reaction on (4-methylphenyl)azo phenyl sulfone **1'b** (entry 15) was carried out in order to confirm that the tosyl substituent in **5** is that of the TosMIC molecule: accordingly, the same imidazole **5b** was obtained both from **1b** and **1'b**.

It is worth noting that, unlike the reactions of **1** with **2**, the formation of imidazole **5** is not accompanied by that of *p*-toluenesulfonamide, which was never detected in the final reaction mixture.[12] Anyway, it would appear that only the Ar-N= fragment of $ArN{=}NSO_2Ar'$ contributes to the framework of the final product **5**. Therefore the fate of the remaining portion of the azosulfone molecule had to be traced and, for this purpose, the experiment of entry 23 was performed on (4-chlorophenyl)azo phenyl sulfone **1'g** in DMF.[13] After aqueous quenching of the reaction and extraction of the 1-(4-chlorophenyl)imidazole **5g** with ether, the aqueous phase was evaporated to dryness and from the residue benzenesulfonylurea **6** was isolated in yield consistent with that of **5g**. Moreover, in all the reactions of Table 2 *p*-toluenesulfinic acid could be isolated from the acidified aqueous phase: the amount in *p*-toluenesulfinic acid, though, was always greater than 1 mole per mole of **5** formed, a fact which can be in part ascribed, as independently ascertained, to some base-induced decomposition[14] of TosMIC in the reaction conditions.

On the grounds of these results and taking into account that two moles of **3** are required per mole of **1'g**, the stoichiometric equation 2 can be written. This, together with equation 3, accounts for the formation of **5g**, of *p*-toluenesulfinic acid and of benzenesulfonylurea **6**, the latter most likely deriving from hydrolysis of benzenesulfonylcyanamide during the aqueous workup.

$$\underset{\mathbf{1'g}}{p\text{-ClC}_6\text{H}_4\text{-N=N-SO}_2\text{Ph}} + \underset{\mathbf{3}}{2\,^{\ominus}\text{CH(NC)(Tos)}} \longrightarrow \mathbf{5g} + \text{Tos}^{\ominus} + (\text{PhSO}_2\text{NCN})^{\ominus} \qquad \text{(eq. 2)}$$

$$(\text{PhSO}_2\text{NCN})^{\ominus} + 2\,\text{H}_2\text{O} \longrightarrow \underset{\mathbf{6}}{\text{PhSO}_2\text{NHCONH}_2} + \text{OH}^{\ominus} \qquad \text{(eq. 3)}$$

Mechanistic features

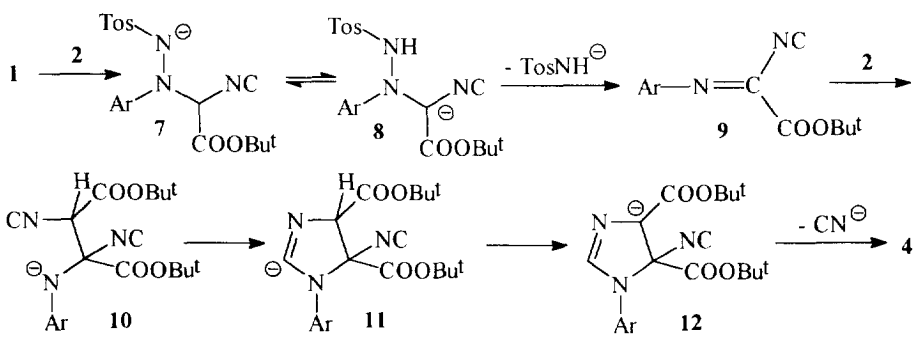
It is envisageable that the reactions of azosulfones **1** with nucleophile **2** initially proceed through steps similar to those of the analogous reactions of **1** with the conjugate bases of other active-methylene compounds.[7] Thus, both the formation of tosylamide and the stoichiometric 1:2 ratio between substrate and nucleophile (eq. 1) are in agreement with the pathway depicted in Scheme 2, featuring two successive attacks of **2**: *a)* on the α nitrogen of **1** and *b)* after elimination of a tosylamide anion from **8**, on the iminic C=N double bond of the resulting intermediate **9**. The parallelism between the system herein and the case of the active-

methylene compounds previously examined[7] should fall down at the level of anion **10**, since the electrophilicity of the isocyano carbon favours intramolecular attack by the negatively charged nitrogen over elimination to a tetrasubstituted ethylene. The resulting imidazoline anion **11** eventually aromatizes to **4** *via* proton shift and elimination of cyanide ion.[15]

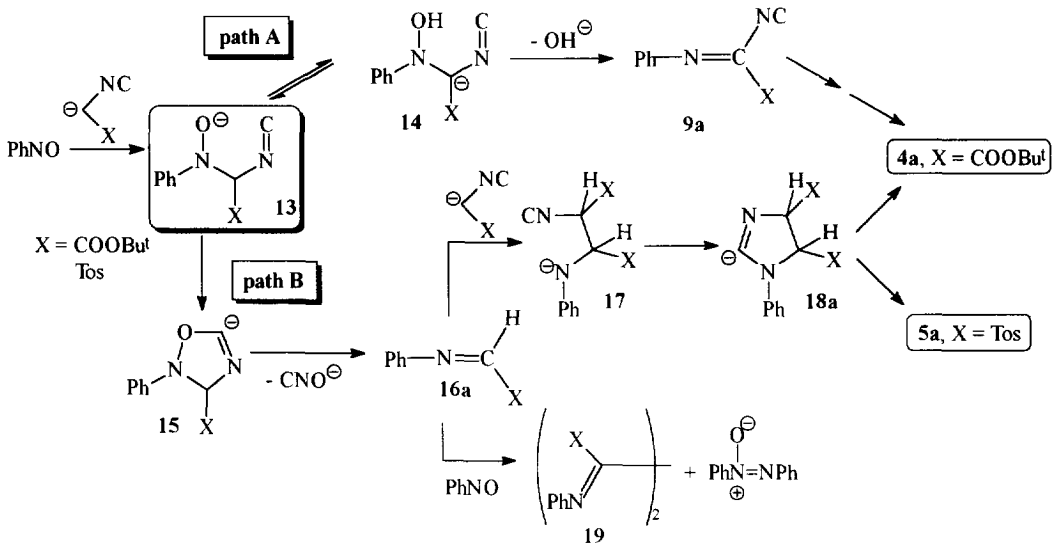
Isolation of the key intermediate **9** would of course represent a compelling mechanistic proof. Unfortunately, this could not be achieved even when starting from equimolar amounts of **1** and **2**: an outcome justifiable, in agreement with previous findings,[7] on the grounds that nucleophilic attack on the iminic double bond of **9** is faster than its formation.

In principle, a different approach to arylimines **9** could be the Ehrlich-Sachs condensation between nitrosoarenes and TBICA. However, some relevant attempts carried out on nitrosobenzene (in the conditions reported[16] for similar condensations with other active-methylene compounds) failed to yield the expected **9** (Ar = Ph). Interestingly enough, also in the conditions usually employed for **1** (*i.e.* Bu^{t}OK/DMSO, with a three-fold excess of nucleophile) the reaction between PhNO and TBICA led to a complex mixture from which only 24% of imidazole **4a** was isolated. Such a result appears not to comply with the alleged[7] synthetic equivalence between azosulfones and nitrosoarenes and can be reasonably interpreted on the grounds of Scheme 3 (X = COOBu^t). The formation of the "expected" arylimine **9a** by elimination of hydroxide is disfavoured with respect to cyclization onto the isocyano group, which is followed by extrusion of cyanate from the intermediate 1,2,4-oxadiazoline anion **15** to yield the alternative iminoderivative **16a**. As a matter of fact, when comparing **7** and **13**, both the lower nucleophilicity of the negatively charged nitrogen *vs.* oxygen and the higher leaving group ability of $TosNH^-$ *vs.* OH^- could well concur in directing the two intermediates towards arylimines **9** ($TosNH^-$ expulsion after proton transfer, Scheme 2) or **16a** (CNO^- extrusion after cyclization), respectively. Furthermore, the latter outcome would be well in keeping with the reported behaviour of carbonyl compounds with the conjugate bases of isonitriles,[17] which results in cyanate ion elimination with C=C double bond formation through a cyclic intermediate of which **15** is the azaanalogue. Within Scheme 3, the formation (although in poor yields) of **4a** from PhNO can be justified by either some concurrence of path A or, within path B, *via* nucleophilic attack onto the arylimine **16a**, cyclization and oxidation of the imidazoline anion **18a** by *e.g.* nitrosobenzene itself. Hints for the actual intervention of the latter route came from the ^{1}H-NMR detection, in mixed chromatographic fractions, of traces of a compound consistent with a 4,5-imidazoline structure;[18] furthermore, the involvement of PhNO as an oxidant could in turn justify the formation of **19**,

Scheme 2



Scheme 3



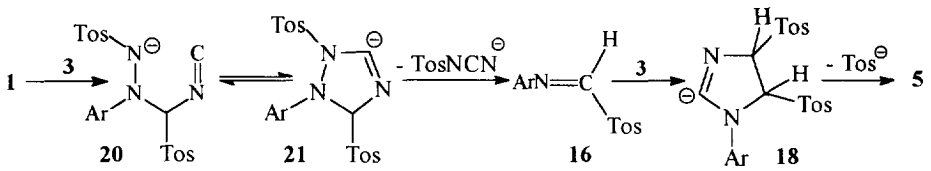
another identified component of the complex final mixture whose yield rises to *ca.* 30% (while that of **4a** drops to almost negligible values) when the reaction is carried out in the presence of excess nitrosobenzene.

With regard to the synthetic equivalence between nitrosoarenes and arylazosulfones, the results of the reactions between the latter and the conjugate base of TosMIC (**3**) should be considered. Notwithstanding the similarity of the two nucleophiles (**2** and **3**) we believe that the formation of the 1-aryl-4-tosylimidazoles **5** together with tosylcyanamide anion (as precursor of the isolated $TosNHCONH_2$) and *p*-toluenesulfinate as coproducts can hardly be justified within the same scheme invoked for the reactions between **1** and **2**. We rather feel that a reasonable hypothesis is represented, in this case, by a sequence analogous to that just described for the reaction between PhNO and **2**, *i.e.* (Scheme 4) cyclization of the initial adduct **20** to **21** (rather than elimination of $TosNH^-$) followed by $TosNCN^-$ extrusion to the arylimine **16** (X = Tos). From the latter intermediate, the formation of the heterocyclic system **5** can be straightforwardly explained *via* further coupling with **3**, cyclization and tosylate expulsion after proton migration. Thus, the key step in the sequence is represented by the cyclization of **20**, possibly favoured (with respect to that of the corresponding intermediate **7** in the reactions of azosulfones with **2**) by the increased electrophilicity of the isocyano carbon due to the nearby strong electronwithdrawing tosyl group.

Most interestingly, the reaction between PhNO and three equivalents of **3** proves to be a more efficient (90% yield) access to **5a** (Scheme 3, X = Tos). This is most likely because the easy **13** to **15** cyclization is coupled with a facile expulsion of the nucleofugic tosyl anion from **18a** following a 1,3 proton shift: an eliminative aromatization route which is precluded to the imidazoline anion deriving from TBICA (**18a**, X = COOBu^t), which less efficiently would collapse to **4a**, as discussed above, *via* oxidative dehydrogenation.

Thus, the results of the reactions with the conjugate base of TosMIC definitely support the previously advanced[7] likelihood of a synthetic equivalence between arylazosulfones and nitrosoarenes: an equivalence which surely deserves deeper investigations in view of the easier accessibility of arylazosulfones.

Scheme 4



In conclusion, while the detailed mechanism of these reactions requires further investigation, they are of synthetic interest, allowing the simple, efficient construction of an azaheterocyclic ring leading to 4,5-bis(*tert*-butoxycarbonyl) and 4-tosyl substituted 1-arylimidazoles.

EXPERIMENTAL

Melting points were determined on a Büchi 535 apparatus and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were taken in $CDCl_3$ (unless otherwise stated) on a Varian Gemini 200 spectrometer; TMS was used as internal standard and chemical shifts are reported as δ values (ppm). IR spectra (nujol mull) were recorded on a Perkin-Elmer 881 infrared spectrophotometer and data are given in cm^{-1}.

Materials

Petroleum ether and light petroleum refer to the fractions with bp 40-60 °C and 80-100 °C, respectively. Dimethylsulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were used as received after storage over molecular sieves (4 Å). Methylene chloride for the synthesis of azosulfones was distilled over P_2O_5 before use. Sodium *p*-toluenesulfinate, sodium benzenesulfinate, potassium *tert*-butoxide, nitrosobenzene, *tert*-butyl isocyanoacetate (TBICA) and tosylmethyl isocyanide (TosMIC) were commercial products used as received.

Column (or preparative plate) chromatographies were performed on silica gel using petroleum ether or appropriate mixtures with CH_2Cl_2, Et_2O or AcOEt as eluants, the solvents being distilled before use.

Arylazosulfones **1a-k**, **1'b**, **1'g**

The title compounds were easily and almost quantitatively obtained from the corresponding arenediazonium salts by coupling with sodium *p*-toluene (**1a-k**) or benzene (**1'b**, **1'g**) sulfinate: as an alternative to the classical procedure involving arenediazonium chlorides in aqueous medium,[19a] we employed, when available in our laboratory, arenediazonium tetrafluoroborates in anhydrous CH_2Cl_2.[19b]

Phenylazo 4-methylphenyl sulfone **1a**, mp 88.6-90.1 °C (EtOH) (lit.,[20] mp 90-91 °C).

(4-Methylphenyl)azo 4-methylphenyl sulfone **1b**, mp 94.5-95.4 °C (EtOH) (lit.,[20] mp 96-97 °C).

(3-Methoxyphenyl)azo 4-methylphenyl sulfone **1c**, mp 77.6-78.9 °C (EtOH) (lit.,[20] mp 84-85 °C).

(4-Methoxyphenyl)azo 4-methylphenyl sulfone **1d**, mp 113.7-114.0 °C (EtOH) (lit.,[20] mp 110-111 °C).

(2-Chlorophenyl)azo 4-methylphenyl sulfone **1e**,[21] mp 110.9-111.4 °C (EtOH); ^{1}H-NMR: 2.48 (3H, s), 7.37 [3H in all, partly overlapped AA' of AA'BB' (*J* 8.3 Hz) and m], 7.51 (2H, m), 7.67 (1H, app. d), 7.84 (2H, BB' of AA'BB', *J* 8.3 Hz). Found: C, 52.9; H, 3.6; N, 9.7% ($C_{13}H_{11}ClN_2O_2S$ requires: C, 53.0; H, 3.8; N, 9.5%).

(3-Chlorophenyl)azo 4-methylphenyl sulfone **1f**,[21] mp 86.3-86.8 °C (EtOH); ^{1}H-NMR: 2.49 (3H, s), 7.49 [4H in all, partly overlapped AA' of AA'BB' (*J* 8.4 Hz) and m], 7.76 (2H, m), 7.86 (2H, BB' of AA'BB', *J* 8.4 Hz). Found: C, 53.0; H, 3.7; N, 9.6% ($C_{13}H_{11}ClN_2O_2S$ requires: C, 53.0; H, 3.8; N, 9.5%).

(4-Chlorophenyl)azo 4-methylphenyl sulfone **1g**, mp 118.7-118.9 °C (EtOH) (lit.,[20] mp 118-119 °C).

(4-Bromophenyl)azo 4-methylphenyl sulfone **1h**, mp 123.3-123.4 °C (EtOH) (lit.,[22] mp 122.0-123.0°C).

(2-Nitrophenyl)azo 4-methylphenyl sulfone **1i**,[21] mp 89.1-89.5 °C (EtOH); ^{1}H-NMR: 2.48 (3H, s), 7.41 and 7.82 (2H each, AA' of AA'BB', *J* 8.3 Hz), 7.52 (1H, m), 7.70 (2H, m), 7.97 (1H, m). Found: C, 51.3; H, 3.7; N, 13.6% ($C_{13}H_{11}N_3O_4S$ requires: C, 51.1; H, 3.6; N, 13.8%).

(4-Nitrophenyl)azo 4-methylphenyl sulfone **1j**, mp 135.0-136.0 °C (EtOH) (lit.,[20] mp 135-136 °C).

(2-Naphthyl)azo 4-methylphenyl sulfone **1k**, mp 113.1-114.8 °C (EtOH); ^{1}H-NMR: 2.49 (3H, s), 7.42 (2H, AA' of AA'BB', *J* 8.2 Hz), 7.61 (2H, m), 7.90 [6H in all, partly overlapped BB' of AA'BB' (*J* 8.2 Hz) and m], 8.42 (1H, s). Found: C, 65.5; H, 4.6; N, 9.1% ($C_{17}H_{14}N_2O_2S$ requires: C, 65.8; H, 4.6; N, 9.0%).

(4-Methylphenyl)azo phenyl sulfone **1'b**, mp 83.9-84.4 °C (EtOH) (lit.,[23] mp 82-83 °C).

(4-Chlorophenyl)azo phenyl sulfone **1'g**, mp 104.6-104.7 °C (EtOH) (lit.,[19b] mp 103-105 °C).

Reactions of arylazosulfones with the potassium salt of TBICA (2) or TosMIC (3)

Reactions were carried out under argon according to a reported general procedure.[3] The nucleophile was generated *in situ* by adding to a slightly cooled solution (*ca.* 5-10 °C) of Bu^{t}OK in DMSO (3 mmol in 10 ml) an equimolar amount of TBICA or TosMIC. After stirring for 30 minutes at room temperature, a solution of the azosulfone **1** in the same solvent (1 mmol in 5 ml) was dropped into the reaction mixture (refrigerated at *ca.* 5-10 °C). Progress of the reaction was followed by TLC and the endpoint estimated (generally after 1-2 h) by the disappearance of **1**.

In the reactions with **2**, the work-up involved pouring of the reaction mixture into ice/brine followed by extraction with Et_2O; the combined extracts were washed with 5% aq. NaOH, with water, and dried (Na_2SO_4); after solvent evaporation under reduced pressure the crude residue was taken-up with petroleum ether and filtered to give pure **4**. Products **4e** and **4j** were isolated by chromatography of the crude residue. Imidazole **4i** was likewise isolated by chromatography, as well as the by-products 2-nitroaniline (10%) and 1-(2-nitrophenyl)-2-tosylhydrazine (16%).

p-Toluenesulfonamide could be isolated and quantified in consistent yield by extracting with ether the basic aqueous phase after acidification. In the case of the reaction with **1i**, a preparative plate chromatography of the residue obtained from evaporation under reduced pressure of ether extracts gave, besides *p*-toluenesulfonamide, 2-nitrophenylurea (10%) and 2-nitrophenylcyanamide (16%).

In the reactions with **3**, the reaction mixture was poured into ice/brine and extracted with Et_2O or CH_2Cl_2; the combined extracts were washed with water and dried (Na_2SO_4); solvent evaporation under reduced pressure and column chromatography of the residue gave the products **5**.

p-Toluenesulfinic acid was isolated by extracting with ether the aqueous phase after acidification. In the case of **1'g**, the reaction mixture was poured into ice/water and extracted with Et_2O; after acidification and extraction of *p*-toluenesulfinic acid, the aqueous phase was evaporated to dryness, the residue taken-up with *ca.* 20 ml of water and extracted repeatedly with CH_2Cl_2. A preparative plate chromatography of the residue obtained after evaporation of the CH_2Cl_2 extracts led to pure benzenesulfonylurea in 55% yield.

Substituted 1-arylimidazoles 4a-k, 5a-h and 5j,k

1-Phenyl-4,5-bis(tert-butoxycarbonyl)imidazole **4a**, mp 113.0-113.6 °C (light petroleum); ^{1}H-NMR: 1.31 (9H, s), 1.61 (9H, s), 7.32 (2H, m), 7.50 (3H, m), 7.56 (1H, s); ^{13}C-NMR: 27.70, 28.22, 81.80, 83.10, 125.76, 128.80, 129.31, 129.40, 136.00, 136.36, 137.81, 158.72, 161.30; IR: 3116 (C-H st.), 1722 (C=O st.), 1598 and 1534 (C=C st.). Found: C, 66.7; H, 7.2; N, 8.1% ($C_{19}H_{24}N_2O_4$ requires: C, 66.3; H, 7.0; N, 8.1%).

1-(4-Methylphenyl)-4,5-bis(tert-butoxycarbonyl)imidazole **4b**, mp 123.4-123.9 °C (petroleum ether); ^{1}H-NMR: 1.33 (9H, s), 1.61 (9H, s), 2.43 (3H, s), 7.19 and 7.28 (2H each, AA'BB', *J* 8.4 Hz), 7.52 (1H, s); ^{13}C-NMR: 21.16, 27.72, 28.22, 81.73, 83.05, 125.49, 128.78, 129.89, 133.40, 136.19, 137.92, 139.45, 158.86, 161.36; IR: 3112 (C-H st.), 1723 (C=O st.), 1590 and 1535 (C=C st.). Found: C, 67.2; H, 7.3; N, 7.8% ($C_{20}H_{26}N_2O_4$ requires: C, 67.0; H, 7.3; N, 7.8%).

1-(3-Methoxyphenyl)-4,5-bis(tert-butoxycarbonyl)imidazole **4c**, mp 113.0-114.0 °C (petroleum ether); ^{1}H-NMR: 1.33 (9H, s), 1.61 (9H, s), 3.83 (3H, s), 6.84 (1H, app. t, *J* 2.2 Hz), 6.90 (1H, m), 7.02 (1H, m), 7.39 (1H, app. t, *J* 8.1 Hz), 7.56 (1H, s); ^{13}C-NMR: 27.73, 28.22, 55.59, 81.81, 83.13, 111.45, 115.05, 117.74, 128.83, 130.18, 136.15, 136.94, 137.68, 158.82, 160.28, 161.26; IR: 3119 (C-H st.), 1720 and 1709 (C=O st.), 1609, 1591 and 1546 (C=C st.). Found: C, 64.0; H, 6.9; N, 7.6% ($C_{20}H_{26}N_2O_5$ requires: C, 64.2; H, 7.0; N, 7.5%).

1-(4-Methoxyphenyl)-4,5-bis(tert-butoxycarbonyl)imidazole **4d**, mp 145.9-146.2 °C (light petroleum); ^{1}H-NMR: 1.34 (9H, s), 1.61 (9H, s), 3.86 (3H, s), 6.97 and 7.24 (2H each, AA'BB', *J* 9.0 Hz), 7.50 (1H, s); ^{13}C-NMR: 27.79, 28.24, 55.68, 81.73, 83.04, 114.44, 127.13, 128.77, 129.03, 136.10, 138.14, 158.91, 160.24, 161.40; IR: 3118 (C-H st.), 1727 and 1705 (C=O st.), 1606 and 1515 (C=C st.). Found: C, 64.6; H, 7.1; N, 7.3% ($C_{20}H_{26}N_2O_5$ requires: C, 64.2; H, 7.0; N, 7.5%).

1-(2-Chlorophenyl)-4,5-bis(tert-butoxycarbonyl)imidazole **4e**, waxy solid; ^{1}H-NMR: 1.27 (9H, s), 1.62 (9H, s), 7.46 (5H in all, partly overlapped m and s); ^{13}C-NMR: 27.61, 28.15, 82.00, 82.82, 127.56, 128.25,

128.80, 130.25, 130.82, 132.00, 134.22, 137.32, 138.37, 157.74, 161.34. Found: C, 59.1; H, 6.4; N, 7.1% ($C_{19}H_{23}ClN_2O_4$ requires: C, 60.2; H, 6.1; N, 7.4%).

1-(3-Chlorophenyl)-4,5-bis(tert-butoxycarbonyl)imidazole **4f**, mp 114.5-115.6 °C (petroleum ether); ^{1}H-NMR: 1.36 (9H, s), 1.61 (9H, s), 7.23 (1H, m), 7.35 (1H, m), 7.46 (2H, m), 7.56 (1H, s); ^{13}C-NMR: 27.75, 28.20, 82.00, 83.42, 123.88, 126.11, 128.42, 129.50, 130.41, 135.16, 136.96, 137.04, 137.64, 158.42, 161.17; IR: 3107 (C-H st.), 1730 and 1708 (C=O st.), 1597 and 1536 (C=C st.). Found: C, 60.3; H, 6.0; N, 7.2% ($C_{19}H_{23}ClN_2O_4$ requires: C, 60.2; H, 6.1; N, 7.4%).

1-(4-Chlorophenyl)-4,5-bis(tert-butoxycarbonyl)imidazole **4g**, mp 147.5-149.0 °C (petroleum ether); ^{1}H-NMR: 1.36 (9H, s), 1.61 (9H, s), 7.27 and 7.47 (2H each, AA'BB', *J* 8.5 Hz), 7.53 (1H, s); ^{13}C-NMR: 27.79, 28.21, 82.03, 83.40, 127.10, 128.31, 129.60, 134.45, 135.47, 137.07, 137.86, 158.52, 161.27; IR: 3113 (C-H st.), 1723 (C=O st.), 1535 (C=C st.). Found: C, 59.9; H, 6.0; N, 7.3% ($C_{19}H_{23}ClN_2O_4$ requires: C, 60.2; H, 6.1; N, 7.4%).

1-(4-Bromophenyl)-4,5-bis(tert-butoxycarbonyl)imidazole **4h**, mp 154.7-155.3 °C (light petroleum); ^{1}H-NMR: 1.36 (9H, s), 1.61 (9H, s), 7.21 and 7.63 (2H each, AA'BB', *J* 8.6 Hz), 7.53 (1H, s); ^{13}C-NMR: 27.75, 28.17, 81.99, 83.40, 123.32, 127.31, 128.18, 132.58, 134.91, 137.01, 137.79, 158.49, 161.21; IR: 3111 (C-H st.), 1715 (C=O st.), 1584 and 1542 (C=C st.). Found: C, 54.1; H, 5.5; N, 6.6 % ($C_{19}H_{23}BrN_2O_4$ requires: C, 53.9; H, 5.5; N, 6.6%).

1-(2-Nitrophenyl)-4,5-bis(tert-butoxycarbonyl)imidazole **4i**, waxy solid; ^{1}H-NMR: 1.30 (9H, s), 1.63 (9H, s), 7.43 (1H, dd, *J* 2.1 and 7.2 Hz), 7.58 (1H, s), 7.75 (2H, m), 8.20 (1H, dd, *J* 1.9 and 7.7 Hz); ^{13}C-NMR: 27.71, 28.17, 82.17, 83.27, 125.56, 127.32, 130.10, 130.73, 133.93, 138.67, 138.73, 145.76, 157.71, 161.31. Found: C, 58.5; H, 5.8; N, 10.5% ($C_{19}H_{23}N_3O_6$ requires: C, 58.6; H, 6.0; N, 10.8%).

1-(4-Nitrophenyl)-4,5-bis(tert-butoxycarbonyl)imidazole **4j**, mp 125.0-126.9 °C (light petroleum); ^{1}H-NMR: 1.40 (9H, s), 1.63 (9H, s), 7.53 and 8.39 (2H each, AA'BB', *J* 8.9 Hz), 7.62 (1H, s); ^{13}C-NMR: 27.83, 28.19, 82.40, 83.89, 124.91, 126.52, 127.49, 137.72, 138.22, 141.01, 147.89, 158.27, 161.07; IR: 3098 (C-H st.), 1730 and 1720 (C=O st.), 1594 and 1527 (C=C st.). Found: C, 59.1; H, 6.1; N, 10.7% ($C_{19}H_{23}N_3O_6$ requires: C, 58.6; H, 6.0; N, 10.8%).

1-(2-Naphthyl)-4,5-bis(tert-butoxycarbonyl)imidazole **4k**, mp 120.3-121.8 °C (light petroleum); ^{1}H-NMR: 1.26 (9H, s), 1.63 (9H, s), 7.40 (1H, dd, *J* 2.1 and 8.6 Hz), 7.59 (2H, m), 7.65 (1H, s), 7.80 (1H, d, *J* 2.1 Hz), 7.90 [3H in all, partly overlapped m and d (*J* 8.6 Hz)]; ^{13}C-NMR: 27.66, 28.21, 81.87, 83.18, 123.40, 124.06, 127.34, 127.51, 127.94, 128.01, 128.84, 129.48, 132.93, 132.98, 133.29, 136.46, 138.04, 158.81, 161.32; IR: 3111 (C-H st.), 1720 and 1710 (C=O st.), 1599 and 1541 (C=C st.). Found: C, 69.5; H, 6.6; N, 7.1% ($C_{23}H_{26}N_2O_4$ requires: C, 70.0; H, 6.6; N, 7.1%).

1-Phenyl-4-tosylimidazole **5a**, mp 159.1-159.8 °C (light petroleum-toluene) [lit.,[24] mp 162-163 °C (MeOH)]; ^{1}H-NMR: 2.42 (3H, s), 7.36 [4H in all, partly overlapped AA' of AA'BB' (*J* 8.4 Hz) and m], 7.49 (3H, m), 7.83 (1H, d, *J* 1.5 Hz), 7.96 (1H, d, *J* 1.5 Hz), 7.99 (2H, BB' of AA'BB', *J* 8.4 Hz); ^{13}C-NMR: 21.63, 121.99, 122.26, 128.11, 128.91, 129.79, 130.25, 136.06, 137.38, 137.83, 143.78, 144.31; IR: 3143 and 3120 (C-H st.), 1595 and 1513 (C=C st.).

1-(4-Methylphenyl)-4-tosylimidazole **5b**, mp 119.8-121.1 °C (light petroleum-toluene); ^{1}H-NMR: 2.42 (6H, s), 7.29 [6H in all, AA'BB' and AA' of AA'BB' (*J* 8.3 Hz)], 7.78 (1H, d, *J* 1.4 Hz), 7.91 (1H, d, *J* 1.4 Hz), 7.98 (2H, BB' of AA'BB', *J* 8.3 Hz); ^{13}C-NMR: 21.05, 21.64, 121.85, 122.36, 128.05, 129.78, 130.69, 133.58, 137.44, 137.76, 139.10, 143.39, 144.28; IR: 3149 and 3106 (C-H st.), 1596 and 1521 (C=C st.). Found: C, 65.6; H, 5.4; N, 9.1% ($C_{17}H_{16}N_2O_2S$ requires: C, 65.4; H, 5.2; N, 9.0%).

1-(3-Methoxyphenyl)-4-tosylimidazole **5c**, mp 118.4-120.3 °C (light petroleum-toluene); ^{1}H-NMR: 2.42 (3H, s), 3.86 (3H, s), 6.88 (1H, m), 6.96 (2H, m), 7.36 [3H in all, partly overlapped AA' of AA'BB' (*J* 8.3 Hz) and m], 7.82 (1H, d, *J* 1.2 Hz), 7.94 (1H, d, *J* 1.2 Hz), 7.98 (2H, BB' of AA'BB', *J* 8.3 Hz); ^{13}C-NMR: 21.64, 55.65, 108.11, 113.99, 114.25, 122.28, 128.10, 129.80, 131.09, 137.05, 137.40, 137.77, 143.63, 144.33, 160.92; IR: 3150 and 3130 (C-H st.), 1596 and 1513 (C=C st.). Found: C, 62.2; H, 4.7; N, 8.6% ($C_{17}H_{16}N_2O_3S$ requires: C, 62.2; H, 4.9; N, 8.5%).

1-(4-Methoxyphenyl)-4-tosylimidazole **5d**, mp 146.5-147.1 °C (light petroleum-toluene); ^{1}H-NMR: 2.42 (3H, s), 3.86 (3H, s), 6.99 and 7.28 (2H each, AA'BB', *J* 9.0 Hz), 7.34 and 7.98 (2H each, AA'BB', *J* 8.1 Hz), 7.73 (1H, d, *J* 1.4 Hz), 7.86 (1H, d, *J* 1.4 Hz); ^{13}C-NMR: 21.63, 55.68, 115.22, 122.70, 123.68, 128.07, 129.13, 129.77, 137.68, 137.85, 143.30, 144.25, 159.93; IR: 3151 and 3120 (C-H st.), 1596 and 1523 (C=C st.). Found: C, 62.3; H, 5.1; N, 8.4% ($C_{17}H_{16}N_2O_3S$ requires: C, 62.2; H, 4.9; N, 8.5%).

1-(2-Chlorophenyl)-4-tosylimidazole **5e**, mp 87.1-87.6 °C (light petroleum); ^{1}H-NMR: 2.43 (3H, s), 7.40 (5H in all, partly overlapped AA' of AA'BB' and m), 7.59 (1H, m), 7.69 (1H, d, *J* 1.5 Hz), 7.85 (1H, d, *J* 1.5 Hz), 7.99 (2H, BB' of AA'BB', *J* 8.4 Hz); ^{13}C-NMR: 21.65, 124.31, 127.54, 128.11, 128.19, 129.80, 130.82, 131.13, 133.61, 137.65, 139.23, 142.97, 144.34; IR: 3140 and 3110 (C-H st.), 1594 and 1509 (C=C st.). Found: C, 57.3; H, 4.1; N, 8.3% ($C_{16}H_{13}ClN_2O_2S$ requires: C, 57.7; H, 3.9; N, 8.4%).

1-(3-Chlorophenyl)-4-tosylimidazole **5f**, mp 169.0-171.0 °C (light petroleum-toluene); ^{1}H-NMR: 2.42 (3H, s), 7.36 [6H in all, partly overlapped AA' of AA'BB' (*J* 8.2 Hz) and m], 7.82 (1H, d, *J* 1.5 Hz), 7.94 (1H, d, *J* 1.5 Hz), 7.98 (2H, BB' of AA'BB', *J* 8.2 Hz); ^{13}C-NMR: 21.67, 120.11, 122.02, 122.33, 128.15, 129.12, 129.85, 131.35, 136.09, 136.98, 137.21, 137.58, 144.22, 144.48; IR: 3151 and 3113 (C-H st.), 1598 and 1514 (C=C st.). Found: C, 57.5; H, 4.2; N, 8.3% ($C_{16}H_{13}ClN_2O_2S$ requires: C, 57.7; H, 3.9; N, 8.4%).

1-(4-Chlorophenyl)-4-tosylimidazole **5g**, mp 180.1-180.6 °C (light petroleum-toluene); ^{1}H-NMR: 2.42 (3H, s), 7.33 and 7.50 (2H each, AA'BB', *J* 8.9 Hz), 7.34 and 7.98 (2H each, AA'BB', *J* 8.2 Hz), 7.79 (1H, d, *J* 1.5 Hz), 7.92 (1H, d, *J* 1.5 Hz); ^{13}C-NMR: 21.64, 122.16, 123.27, 128.09, 129.82, 130.44, 134.49, 134.89, 137.30, 137.58, 144.01, 144.45; IR: 3124 (C-H st.), 1597 and 1519 (C=C st.). Found: C, 57.6; H, 3.9; N, 8.4% ($C_{16}H_{13}ClN_2O_2S$ requires: C, 57.7; H, 3.9; N, 8.4%).

1-(4-Bromophenyl)-4-tosylimidazole **5h**, mp 186.3-187.1 °C (light petroleum-toluene); ^{1}H-NMR: 2.42 (3H, s), 7.27 and 7.65 (2H each, AA'BB', *J* 8.8 Hz), 7.34 and 7.97 (2H each, AA'BB', *J* 8.1 Hz), 7.80 (1H, d, *J* 1.4 Hz), 7.93 (1H, d, *J* 1.4 Hz); ^{13}C-NMR: 21.64, 122.04, 122.70, 123.49, 128.11, 129.82, 133.42, 134.99, 137.21, 137.59, 144.11, 144.44; IR: 3123 (C-H st.), 1592 and 1517 (C=C st.). Found: C, 49.9; H, 3.3; N, 7.5% ($C_{16}H_{13}BrN_2O_2S$ requires: C, 50.9; H, 3.5; N, 7.4%).

1-(4-Nitrophenyl)-4-tosylimidazole **5j**, mp 233.1-233.7 °C (toluene) (lit.,[24] mp 236-237 °C); ^{1}H-NMR: 2.43 (3H, s), 7.36 and 7.98 (2H each, AA'BB', *J* 8.2 Hz), 7.60 and 8.42 (2H each, AA'BB', *J* 9.0 Hz), 7.94 (1H, d, *J* 1.5 Hz), 8.05 (1H, d, *J* 1.5 Hz); ^{13}C-NMR: 21.70, 121.50, 122.06, 125.95, 128.18, 129.86, 136.96, 137.22, 140.54, 144.68, 145.13, 147.36; IR: 3130 (C-H st.), 1598 and 1521 (C=C st.).

1-(2-Naphthyl)-4-tosylimidazole **5k**, mp 139.6-140.1 °C (light petroleum-toluene); ^{1}H-NMR: 2.43 (3H, s), 7.35 (2H, AA' of AA'BB', *J* 8.1 Hz), 7.48 (1H, dd, *J* 2.2 and 8.8 Hz), 7.60 (2H, m), 7.83-8.07 [8H in all, m, d (*J* 1.5 Hz) and d (*J* 1.5 Hz)]; ^{13}C-NMR: 21.62, 119.95, 120.21, 122.46, 127.31, 127.85, 128.00, 128.11, 129.81, 130.63, 132.77, 133.31, 137.61, 137.78, 143.80, 144.34; IR: 3155 and 3130 (C-H st.), 1595 and 1507 (C=C st.). Found: C, 68.9; H, 4.6; N, 8.1% ($C_{20}H_{16}N_2O_2S$ requires: C, 69.0; H, 4.6; N, 8.0%).

Other compounds

2-Nitroaniline, *p*-toluenesulfonamide and *p*-toluenesulfinic acid were identified by comparison with authentic samples.

Benzenesulfonylurea **6**, mp 167.2-169.0 °C (EtOH) [lit.,[25] mp 169 °C (EtOH)]; ^{1}H-NMR (DMSO-d_6): 6.40 (2H, br s), 7.63 (3H, m), 7.90 (2H, m), 10.62 (1H, br s); ^{13}C-NMR (DMSO-d_6): 126.98, 128,90, 133.01, 140.17, 151.96; IR: 3418, 3284 and 3206 (NH st.), 1657 (C=O st.).

2-Nitrophenylcyanamide, mp 146.5-147.0 °C (lit.,[26] mp 146 °C); ^{1}H-NMR: 7.23 (1H, app. td), 7.54 (1H, dd, *J* 1.4 and 8.3 Hz), 7.74 (1H, app. td), 8.29 (1H, dd, *J* 1.5 and 8.5 Hz), 9.47 (1H, br s); IR: 3209 (NH st.), 2252 (CN st).

1-(2-Nitrophenyl)-2-tosylhydrazine, mp 194.3-194.5 °C (light petroleum-toluene); ^{1}H-NMR: 2.45 (3H, s), 6.32 (1H, br s), 6.87 (1H, m), 7.36 and 7.80 (2H each, AA' of AA'BB', *J* 8.2 Hz), 7.53 (2H, m), 8.12 (1H, app. dd, *J* 1.4 and 8.6 Hz), 8.85 (1H, br s);^{13}C-NMR (DMSO-d_6): 20.99, 115.73, 118.67, 125.52, 127.64, 129.80, 132.06, 134.31, 136.19, 144.10, 144.58; IR: 3329 and 3216 (NH st.), 1612 and 1577 (C=C st). Found: C, 50.5; H, 4.2; N, 13.9% ($C_{13}H_{13}N_3O_4S$ requires: C, 50.8; H, 4.3; N, 13.7%).

2-Nitrophenylurea, mp 178.0-179.2 °C (MeOH) [lit.,[26] mp 181 °C (MeOH)]; ^{1}H-NMR: 4.91 (2H, br s), 7.10 (1H, app. td), 7.62 (1H, app. td), 8.19 (1H, d, *J* 8.6 Hz), 8.62 (1H, d, *J* 8.8 Hz), 9.8 (1H, br s); ^{13}C-NMR (DMSO-d_6): 121.66, 122.41, 125.39, 135.00, 135.96, 137.35, 155.22; IR: 3400, 3340 and 3220 (NH st.), 1679 (CO st.).

Reactions on 4b for structural assignment

1-(4-Methylphenyl)-4,5-imidazoledicarboxylic acid was obtained from imidazole **4b** (1 mmol), by treatment in dry CH_2Cl_2 (15 ml) with CF_3SO_3H (1.3 mol. equiv.) overnight at room temperature. The crude product, which separated as a white solid (80% yield), was filtered, washed with water and used for the following reaction; mp 263.5-264.0 °C (dec.); ^{1}H-NMR (DMSO-d_6): 2.39 (3H, s), 7.31 and 7.38 (2H each, AA'BB', *J* 8.6 Hz), 8.85 (1H, s), *ca.* 11 (2H, br s); ^{13}C-NMR (DMSO-d_6): 20.58, 125.88, 128.20, 129.19, 132.04, 133.15, 138.84, 138.94, 158.73, 161.23; IR: 3130 (C-H st.), 2559 (COO-H st.), 1721 (C=O st.).

1-(4-Methylphenyl)-4-(phenylcarbamoyl)imidazole was obtained by refluxing under magnetic stirring a solution of the above diacid (0.5 mmol) in freshly distilled aniline (5 ml) following a procedure already reported for 1-methyl-4,5-imidazoledicarboxylic acid.[8] At the end of the reaction, aniline was removed by distillation at reduced pressure; the residue, which crystallizes as white needles by addition of petroleum ether, was filtered and washed with petroleum ether on the filter. 1-(4-Methylphenyl)imidazole-4-carbanilide was then crystallized from light petroleum-toluene, mp 189.4-190.4 °C; ^{1}H-NMR: 2.43 (3H, s), 7.12 (1H, app. t), 7.33 (6H in all, partly overlapped s and m), 7.73 (2H, app. d), 7.78 (1H, d, *J* 1.4 Hz), 7.97 (1H, d, *J* 1.4 Hz), 8.99 (1H, br s); ^{13}C-NMR: 21.03, 119.61, 121.58, 123.95, 129.02, 130.62, 134.22, 135.04, 138.04, 138.54, 160.21. Found: C, 73.3; H, 5.4; N, 15.4% ($C_{17}H_{15}N_3O$ requires: C, 73.6; H, 5.5; N, 15.2%).

Reactions of nitrosobenzene with the potassium salt of TBICA (2) or TosMIC (3)

Reactions were carried out according to the procedure described for azosulfones. Nitrosobenzene (1 mmol) in 5 ml of DMSO was added to the nucleophile solution (generated *in situ*, 1 or 3 mmol in 10 ml of DMSO) cooled at *ca.* 5-10 °C. The work-up involved pouring of the reaction mixture into ice/brine; pH was adjusted to neutrality with 3% HCl before the extraction with Et_2O; the combined extracts were washed with water and dried (Na_2SO_4); solvent evaporation under reduced pressure and column chromatography of the residue allowed isolation of pure products. In those cases in which compound **19** (X = COOBu^t) was present, it was isolated as a solid by filtration of the concentrated ethereal solution, before the chromatographic separation.

Azoxybenzene was confirmed by comparison (mixed mp and ^{1}H-NMR data) with an authentic sample.

Di-tert-butyl 2,3-bis(phenylimino)succinate **19** (X = COOBu^t), mp 191.6-192.4 °C (light petroleum); the ^{1}H-NMR showed the presence, in solution, of two stereoisomers **A** and **B** (58:42 molar ratio): 1.34 [9H (**A**), s], 1.54 [9H (**B**), s], 6.59 [2H (**B**), app. dd], 7.21 [5H (**A**) and 3H (**B**), m]; ^{13}C-NMR: 27.93, 84.17, 119.97 (**B**), 120.10 (**A**), 126.10 (**A**), 126.68 (**B**), 128.67 (**A**), 128.79 (**B**), 147.53 (**B**), 148.43 (**A**), 156.80 (**B**), 158.52 (**A**), 160.51 (**B**), 161.92 (**A**); IR: 1722 (C=O st.). Found: C, 70.6; H, 7.0; N, 7.0% ($C_{24}H_{28}NO_4$ requires: C, 70.6; H, 6.9; N, 6.9%).

Acknowledgements. Financial support from M.U.R.S.T. and CNR/Rome are gratefully acknowledged. We thank Miss M. T. Scrivani for skilful contribution.

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(*Received in UK* 29 *October* 1996; *revised* 26 *November* 1996; *accepted* 28 *November* 1996)