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Azoles. Part 43:[1] Reactions of *N*-(Phenylsulphonylmethyl)- and *N*-(Phenylsulphinylmethyl)azoles with some Nitroarenes

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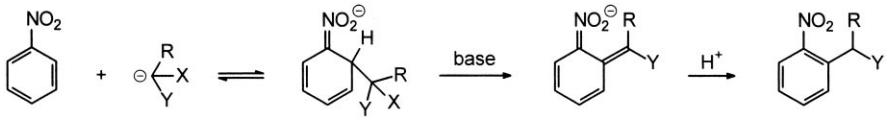
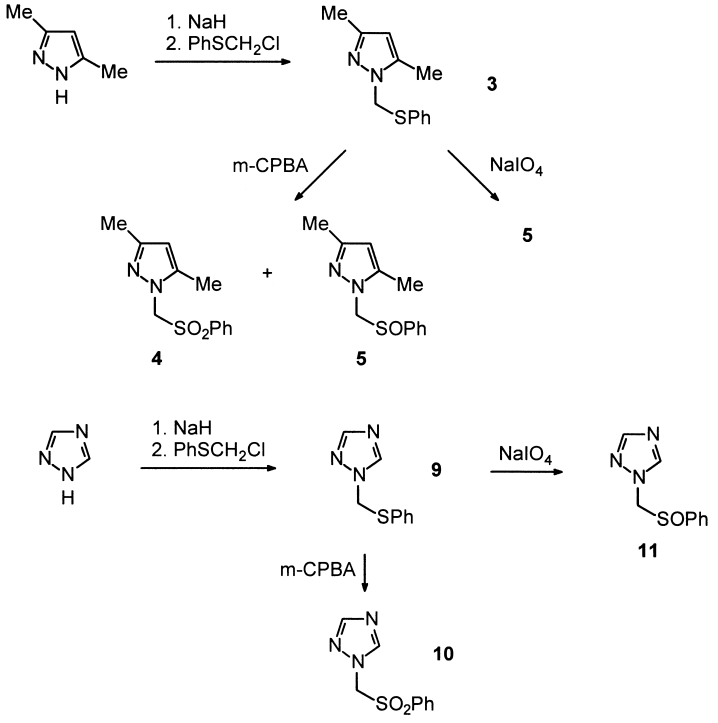
Abstract—Treatment of nitroarenes with 1-(phenylsulphonylmethyl)azoles in the KOH/DMSO system at room temperature resulted usually in the cleavage of the phenylsulphonyl group, whereas the *t*-BuOK/DMF system at low temperature promotes to a greater extent oxidation of the σ-adducts. When 1-(phenylsulphinylmethyl)azoles were used for the reaction only elimination of the phenylsulphinyl group was observed.



Scheme 1.



Scheme 2.

Keywords: azoles; sulfones; sulfoxides; vicarious nucleophilic substitution.

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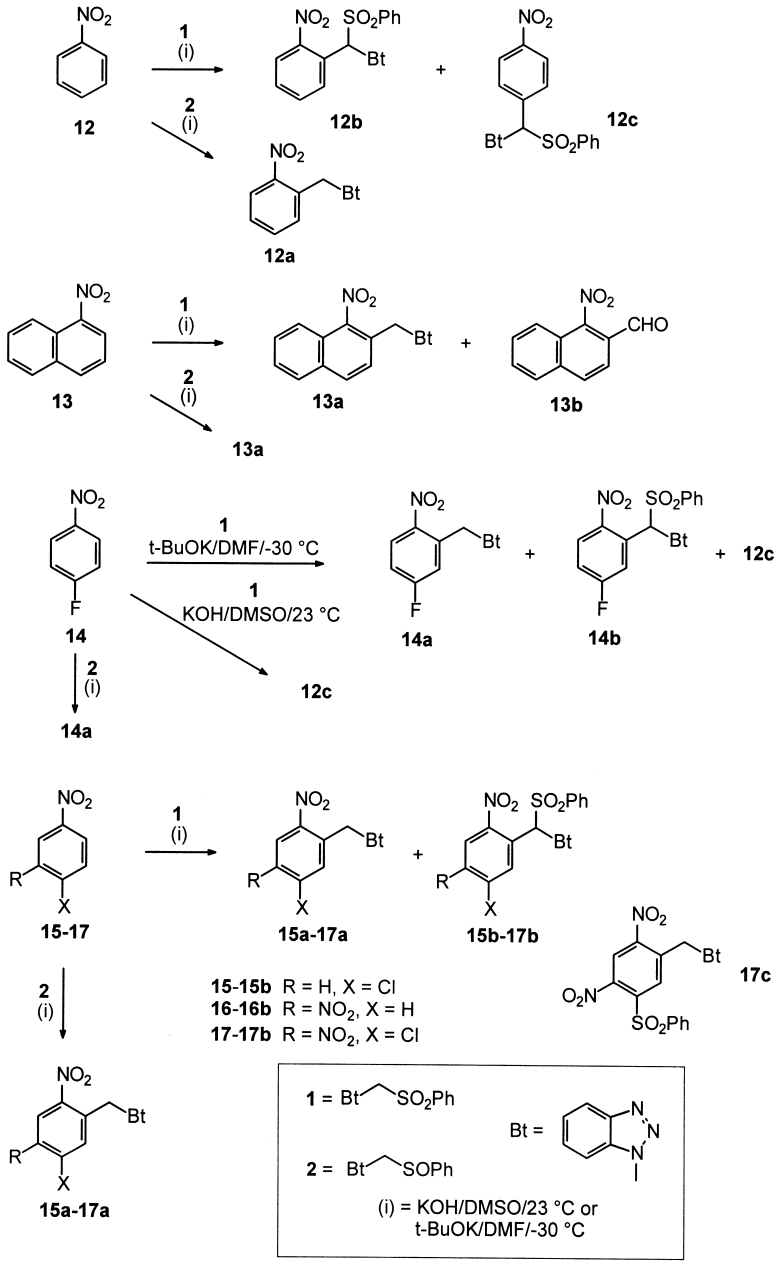


Scheme 3.

The vicarious nucleophilic substitution (VNS) of hydrogen, also called the Mąkosza reaction, is a versatile method for the introduction of a variety of substituents into electrophilic arenes.[2,3] The reaction is also a useful tool for building heterocyclic rings.[4] The VNS of hydrogen is a two-step reaction proceeding via fast and reversible formation of the σ-adducts, followed by slower, base-induced β-elimination (Scheme 1, only the *ortho* isomer is shown).[2]

In continuation of my studies on nucleophilic substitution in azoles[5] I investigated the VNS of hydrogen using carbanions of some 1-(phenylsulphonylmethyl)- and 1-(phenylsulphinylmethyl)azoles **1**, **4**, **7**, **10** and **2**, **5**, **8**, **11**, respectively.[6]

The benzotriazole and benzimidazole derivatives **1**, **2** and **7**, **8** were obtained according to known procedures.[7,8] However, oxidation of 1-(phenylthiomethyl)benzimidazole (**6**) with *m*-chloroperoxybenzoic acid (*m*-CPBA) at 0°C gave both 1-(phenylsulphonylmethyl)- and 1-(phenylsulphinylmethyl)benzimidazole **7** and **8** that required separation by chromatography.

The pyrazole and triazole derivatives **4**, **5** and **10**, **11** were obtained in a two-step synthesis (Scheme 2). Sodium salts of 3,5-dimethylpyrazole or 1,2,4-triazole were treated with chloromethyl phenyl sulphide to give phenylthiomethyl derivatives **3** or **9**. Oxidation of compound **3** with *m*-CPBA led to both sulphone **4** and sulphoxide **5**, whereas oxidation of compound **9** with the same reagent provided only the sulphone **10**. On the other hand, the sulphoxides **5** and **11** could be obtained by oxidation of the sulphides **3** and **9** with $NaIO_4$.

Table 1. Products of the reaction of nitroarenes **12**–**23** with compounds **1** or **2**

Nitroarene	Products	Yields (%)			
		Starting material: **1**		Starting material: **2**	
		Method A[a]	Method B	Method A	Method B
12	**12a**	0	0	7 (30)[b]	20
	12b	Traces[c]	4	–	–
	12c	Traces	2	–	–
13	**13a**	39	25	33 (30)	50
	13b	2	4	3	3
14	**14a**	0	31	44	63
	14b	0	8	–	–
	12c	52	14	–	–
15	**15a**	49	11	10	47
	15b	Traces	41	–	–
	12c	6	11	–	–
16	**16a**	71	4	65 (10)	38 (5)
	16b	0	45	–	–
17	**17a**	49	4	38 (5)	22 (5)
	17b	2	37	–	–
	17c	6	8	–	–
18	**18a**	0	0	68 (50)	20
	18b	3	0	–	–
19	**19a**	Traces	Traces	82	31
	19b	41	45	–	–
20	**20a**	0	0	61	20 (35)
21	**21a**	48	5	54 (60)	26
	21b	0	Traces	–	–
22	**22a**	72	6	64	63
	22b	0	15	–	–
23	**23a**	48	20	46	37
	23b	2	9	–	–

[a] Method A: KOH/DMSO/23°C; method B: *t*-BuOK/DMF/−30°C.
[b] The reaction time (min), if different from the values in the Experimental part, is given in brackets.
[c] Traces means yields less than 2%, usually of not isolated compounds.

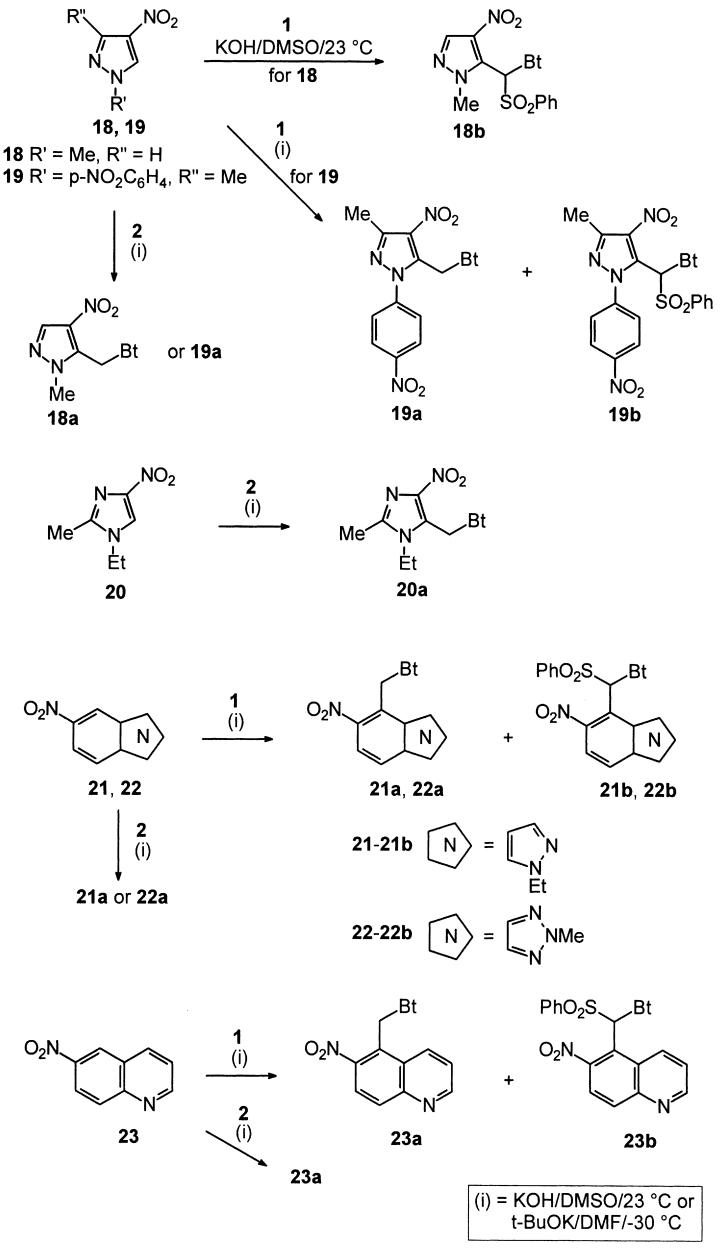
Particularly interesting is 1-(phenylsulphonylmethyl)benzotriazole (**1**) for the benzotriazolate anion is regarded as a good leaving group that can be used in place of halogen in many reactions.[9] Hence, one could expect the benzotriazolate anion to leave in the course of the VNS. This assumption was confirmed by a recent work of Katritzky and Xie who demonstrated that tris(benzotriazol-1yl)-methane could act as an efficient reagent for introduction of the bis(benzotriazol-1-yl)methyl group into nitroarenes.[10] Moreover, Katritzky and Toader showed the utility of diarylmethylbenzotriazoles for the synthesis of *p*-(nitroaryl)diarylmethanes via the VNS of hydrogen.[11] The benzotriazolate anion also acted as a leaving group in that case.

However, when the reactions of sulphone **1** and nitroarenes (Scheme 3, Table 1) or nitroheteroarenes (Scheme 4, Table 1) were carried out in the KOH/dimethylsulphoxide base/solvent system at room temperature (abbreviated further in the text to 'KOH/DMSO system') no expected products of the VNS, i.e. compounds containing only the phenylsulphonylmethyl substituent, were found in the reaction mixtures. Instead the phenylsulphinate anion was eliminated and products with the benzotriazolylmethyl residue (the VNS products) were isolated from the reaction mixtures. Another type of compound was also detected in the reaction mixtures. The compounds were identified as products of oxidation of the σ-adducts. This kind of conversion of the σ-complexes is known as oxidative nucleophilic substitution of hydrogen (ONSH).[12–15] Although the VNS products usually prevailed, the ratio of both products depends on the nature of the starting nitroarene and the reaction conditions. The ONSH products were obtained in higher yields, and even in some cases were the major products, when the reactions were performed in the *t*-BuOK/dimethylformamide (DMF) system at −30°C (abbreviated further in the text to '*t*-BuOK/DMF system'). The final outcome of the reaction was controlled to a large extent by electrophilic strength of the nitroarene. The reaction gave reasonable to good yields when strong electrophiles, like 1-chloro-4-nitrobenzene (**15**), 1,3-dinitrobenzene (**16**) and its chloro derivative **17**, or such nitroheteroaromatics like derivatives of pyrazole **19** and benzotriazole **22**, were used as starting materials (Schemes 3 and 4, Table 1). In all these cases but **19** the reaction pattern was as follows: the VNS products **15a**–**17a** and **22a** were the sole or predominant compounds in the KOH/DMSO system, and the ONSH products **15b**–**17b** and **22b** prevailed in the *t*-BuOK/DMF one. A different kind of compound, namely **17c**, resulted from the aromatic nucleophilic substitution (S_NAr) of the chlorine atom by the phenylsulphinate ion, was isolated in 6–8% yield from the reaction of **1** and **17** in both systems. Compound **17c** was also obtained in 67% yield by treatment of the benzotriazole derivative **17a** with sodium benzenesulphinate in DMSO. This way of preparation of compound **17c** constitutes an additional proof for both its structure and possibility of its formation under the VNS conditions. Furthermore, another product of the substitution of the chlorine atom, namely compound **16b**, was detected in the same reaction mixture but its attempted isolation was unsuccessful.

Only the ONSH product **19b** was isolated from the reaction mixture of **19** and **1** in both systems (Scheme 4, Table 1). However, the ^{1}H NMR spectrum of one of the chromatographic fractions from the reaction carried out in the KOH/DMSO system did reveal signals corresponding to the VNS product, but I was not able to isolate it in a pure form due to its low yield (approximately 2%) and contamination with a few side-products of close polarity.

1-Fluoro-4-nitrobenzene (**14**) was an exception among the reactive species. When compound **14** was treated with sulphone **1** in the KOH/DMSO system (Scheme 3, Table 1), only one compound, namely the product of fluorine substitution **12c**, was found in the reaction mixture in 52% yield. However, the reaction in the *t*-BuOK/DMF system afforded three compounds: the VNS (the major product), ONSH and fluorine substitution products **14a**, **14b** and **12c**, respectively. It should be herein added that the product of halogen substitution (compound **12c**) was also isolated from the reaction of 1-chloro-4-nitrobenzene (**15**) and sulphone **1**, but its yield in the KOH/DMSO system was much lower (6%).

The VNS and ONSH products can be easily distinguished by their ^{1}H NMR spectra. The singlet for the methine proton in the ONSH products appears at much higher frequencies (between 8 and 9 ppm) than the one for the methylene proton in the VNS products (between 6.1 and 6.6 ppm). The benzotriazole protons 5-H and 6-H are observed at about 7.5 ppm as threefold doublets with two *ortho*



Scheme 4.

couplings (8.5 and 7 Hz) and one *meta* coupling (1 Hz). The remaining protons 4-H and 7-H should give also the same pattern, that is threefold doublets with *ortho*, *meta* and *para* couplings. However, owing to a small difference between the latter two couplings (both are approximately 1 Hz) and the large half-width, the signals are not well resolved and appear usually as a doublet of pseudotriplets, sometimes even as distorted doublets (in the Experimental part these signals are designated as multiplets). In the spectra of the VNS products these signals can be seen at higher frequencies (ca. 8 ppm) than the 5-H and 6-H threefold doublets, but in the spectra of the ONSH products the signal for the 7-H proton is shifted strongly upfield to ca. 7.2 ppm. This shift can be attributable to the location of the 7-H proton in the shielding zone of the tosyl group.

The singlets at 8.96 and 9.07 ppm in the ^{1}H NMR spectrum of **17b** were assigned to the 3-H and 6-H protons of the dinitrobenzene ring, respectively, using NOE difference spectroscopy. Irradiation of the methine proton (8.27 ppm) resulted in enhancement of both 3-H and 6-H protons, but the signal at 9.07 ppm was enhanced about four times stronger, so it was assigned to the closer 6-H proton.

The outcome of the reaction with less electrophilic arenes was not predictable. Upon treatment with sulphone **1** in the KOH/DMSO system nitrobenzene (**12**) gave several products, but I was not able to isolate any pure compound. The reaction in the *t*-BuOK/DMF system led to a similar mixture of compounds from which only the ONSH product **12b** was isolated in 4% yield. I unsuccessfully tried to shift the reaction course toward the ONSH products by passing oxygen through the reaction mixture in the *t*-BuOK/DMF system (method D). The slow reacting carbanion of **1** was

eliminated quickly from the reaction medium and after 30 min the reaction mixture consisted mainly of tars that prevented isolation of any pure product. Besides, the application of $KMnO_4$ in liquid ammonia according to van der Plas and Woźniak[15,16] was ineffective for oxidation of the σ-adducts due to low solubility of sulphone **1** in this medium. Using 10-fold excess of nitrobenzene (**12**) or prolongation of the reaction time did not lead to isolable compounds either.

The reaction of **1** with 1-nitronaphthalene (**13**) in both base/solvent systems provided only two products **13a** and **13b** (Scheme 3, Table 1). The VNS product **13a**, substituted at the *ortho* position in respect to the nitro group, was obtained in a moderate yield (25–39%). The *ortho* substitution was confirmed by large coupling constants for doublets of the 3-H and 4-H protons (J=8.6 Hz), and also by an NOE difference experiment. Upon irradiation of the methylene group resonance the difference spectrum showed enhancement of the 3-H doublet and also the multiplet (distorted doublet) of the 7-H proton of the benzotriazole ring. The remaining protons of the naphthalene ring were unaffected. A similar preference for the *ortho* substitution, even in the KOH/DMSO system, was observed in the VNS of 1-nitronaphthalene (**13**) and chloromethyl *p*-tolyl sulphone.[17] This fact was explained by higher energy of the *para* σ-adduct in comparison with the *ortho* one. Another product, compound **13b**, was isolated in a low yield (2–4%) from the reaction mixtures of **1** and **13** in both systems. The high resolution mass spectrum shows that the exact mass for the molecular ion is 201.0432 Da/charge which corresponds to a formula of $C_{11}H_7NO_3$. The IR spectrum reveals a strong carbonyl band at 1692 cm^{-1} and another intense band close to 1500 cm^{-1}. The latter one can be assigned to a nitro group. The ^1H NMR spectrum in the 7.8–8.5 ppm region is consistent with a 1,2-substituted nitronaphthalene, and a singlet at 10.17 ppm may represent an aldehyde proton. On the basis of the above data and literature information[18,19] the structure of compound **13b** was established as 1-nitronaphthalene-2-carboxaldehyde.

1-Ethyl-5-nitroindazole (**21**) behaved similarly to compound **13** upon treatment with sulphone **1** giving only the VNS product **21a** in the KOH/DMSO system. Although the reaction in this system led to an acceptable yield (45%) of **21a**, the reaction in the *t*-BuOK/DMF system was dominated by tars and the yield of **21a** dropped to 5%. In the latter system the presence of small amounts of the ONSH product **21b** could not be excluded.

Treatment of compounds **18** and **20** with sulphone **1** (Scheme 4, Table 1) gave unacceptable results regardless of the system used. The prolongation of the reaction time led to slow decomposition of the starting materials. Only the ONSH product **18b** was isolated in a poor yield (3%) from the reaction carried out in the KOH/DMSO system.

The reaction of 5-nitroquinoline (**23**) and **1** afforded the VNS product **23a** as a major component of the reaction mixture in both base/solvent systems (Scheme 4, Table 1). Although a bit more of the ONSH product **23b** was produced in the method B, its yield was low in both systems.

From the above described results the following conclusions can be drawn.

First, the benzotriazolate anion is indeed a poorer leaving group in the VNS of hydrogen than the phenylsulphinate.

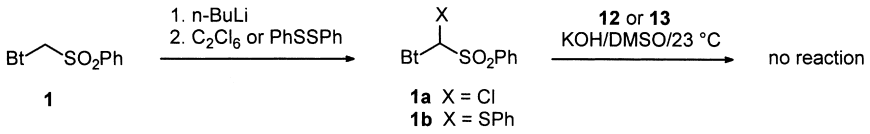
Second, more preference for the oxidation of the σ-adducts in the *t*-BuOK/DMF system in comparison with the KOH/DMSO one reflects greater stabilization of these adducts in this system. It seems that the course of the reaction with sulphone **1** shows some similarities to the VNS in which tertiary carbanions enter the *ortho* position to the nitro group in analogous conditions.[20] Marginally successful efforts were made to find a principal factor in the oxidation of the σ-complexes. The reaction of sulphone **1** and 1-chloro-4-nitrobenzene (**15**) carried out under argon in deoxygenated DMF according to the method B still led to both VNS and ONSH products **15a** and **15b**. Albeit the yield of **15b** dropped a bit from 41 to 32%, the yield of **15a** was again very low (4%). It means that apart from the oxygen dissolved in a solvent also other factors, like transfer of oxygen from nitroarene, may play an important role in the oxidation of the σ-adducts.

When tetrahydrofuran was used instead of dimethylformamide in the method B (method E), the reaction rate was significantly slower and after 90 min most of the starting materials used in this experiment, i.e. compounds **15** and **1**, were unchanged in the reaction mixture.

Third, the process that is hindered in the reaction is the elimination step. The elimination in the VNS proceeds via a transition state involving the anti arrangement of the proton being abstracted by the base and the leaving group. Moreover, transfer of charge to the leaving group is assisted by its delocalization in the sulphonyl moiety. This would require both oxygen atoms of the sulphonyl group to adopt a gauche orientation with respect to the forming double bond, exactly like it has been determined for α-sulphonyl carbanions, where the lone pair of electrons is placed gauche to the two sulphonyl O atoms.[21] A bulky substituent, like the benzotriazole moiety, pushes the sulphonyl group out of this orientation and therefore retards the elimination step. As was mentioned in the introduction, the first step of the VNS of hydrogen is the fast and reversible formation of σ-adducts. When highly electrophilic compounds, like **16**, **17** or **22**, are subjected to the reaction, the equilibrium of the first step is strongly shifted toward the σ-adducts, so their concentration is high enough to ensure satisfactory yields of the VNS or even ONSH products. However, when compounds of comparatively low electrophilicity, like pyrazole **18** or imidazole **20**, are used in the reaction, the concentration of the σ-adducts is insufficient for the elimination or oxidative removal of hydrogen.

Bulkiness of the base has no significant effect on the elimination. Using *t*-BuOK instead of KOH (DMSO as a solvent, method C) led to similar results like in method A. For example, from the reaction of compounds **15** and **1**, according to method C, I isolated 45% of **15a** and 7% of **12c**.

The hindered elimination step changed the reaction course



Scheme 5.

in these cases where conventional S_NAr is possible. Thus in the KOH/DMSO system 1-fluoro-4-nitrobenzene (**14**) gave only compound **12c** resulted from the exchange of the fluorine atom. The S_NAr products were also isolated from the reaction mixtures of sulphone **1** and 1-chloro-4-nitrobenzene (**15**) (compound **12c**) or 1-chloro-2,4-dinitrobenzene (**17**) (compound **16b**). This constitutes an additional proof for the hindrance of the elimination step as the VNS of hydrogen is known to occur faster at carbons bearing hydrogen atoms than at those connected with other substituents. For example, the S_NAr of halogen occurred to a negligible extent in comparison with the VNS of hydrogen even for 1-fluoro-2,4-dinitrobenzene containing an easily replaceable fluorine atom.[22]

The assumption of the hindrance of the elimination step was further confirmed by unsuccessful attempts to react tertiary carbanion precursors **1a** and **1b**, containing additional leaving groups, with some nitroarenes (Scheme 5).

The carbanion precursors **1a** and **1b** were obtained by lithiation of sulphone **1** and subsequent reactions with hexachloroethane or diphenyl disulphide. Compounds **1a** and **1b** were subjected to the VNS of hydrogen with nitrobenzene (**12**) or 1-nitronaphthalene (**13**). Regardless of the system base/solvent used only starting materials were recovered from the reaction mixtures or, when more drastic conditions were applied, decomposition of the carbanion precursors **1a** or **1b** was observed. Steric repulsion between the substituents in the σ-adduct effectively prevented their suitable arrangement for elimination.

On the basis of the above discussion it is clear why the VNS for nitropyrazole **19** led to such poor yield of the VNS product **19b**. Coplanar alignment of the pyrazole and phenyl rings (the advantageous arrangement)[23] prohibits attainment of the anti conformation because of the steric repulsion between the benzotriazole residue and the phenyl (or nitro) group. When both rings are noncoplanar, the phenyl ring forces the sulphonyl group out of the favourable gauche conformation.

On the other hand, the reaction of sulphone **1** and nitroindazole **21** led only to the VNS product **21a** because of the favourable for elimination geometry around the reaction centre.

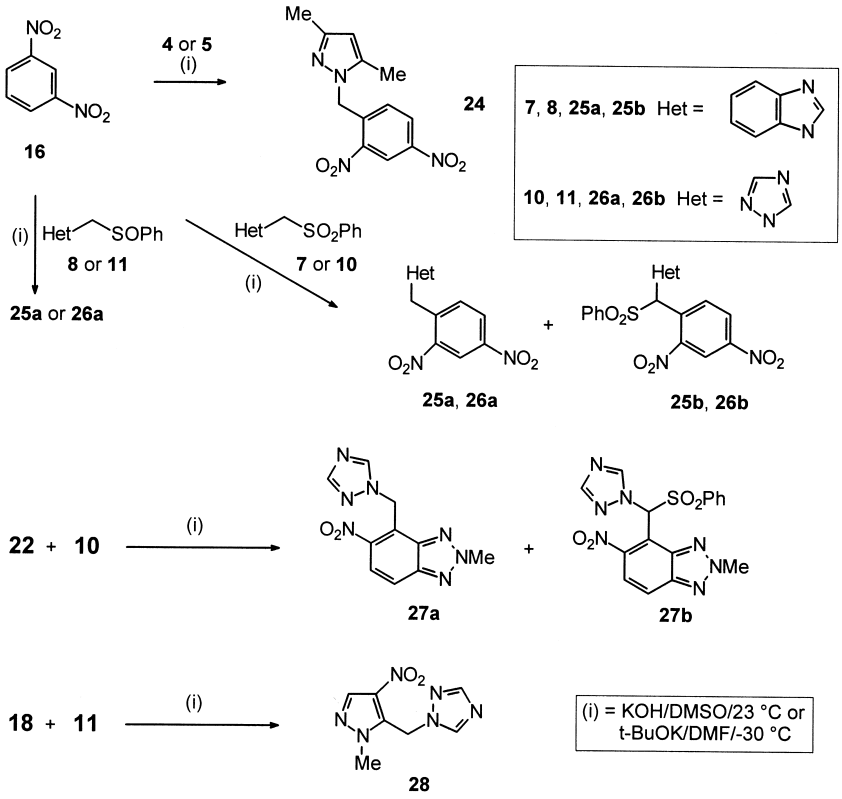
A similar preference for the VNS product **13a** in the reaction of sulphone **1** and 1-nitronaphthalene (**13**) may be connected with instability of the initially formed ONSH product under the reaction conditions. The latter product probably undergoes transformation into, inter alia, aldehyde **13b**. Although compound **13b** could result from hydrolysis of the ONSH product in a similar way to the already described synthesis of aromatic aldehydes from bis(benzotriazol-1-yl)methyl or dihalomethyl nitroarenes,[10,19] the participation of the neighbouring nitro group may play a key role in its formation.

A further evidence for the above described hindrance in the elimination step provided a series of reactions I performed using sulphoxide **2** and nitroarenes **12**–**23** (Schemes 3 and 4, Table 1). Either in the KOH/DMSO or *t*-BuOK/DMF system only the VNS products **12a**–**23a** were isolated from the reaction mixtures. Analysis of the ^1H NMR spectra of the reaction mixtures did not reveal signals corresponding to the ONSH products as well as compounds resulted from the nucleophilic substitution of halogen. The reaction was very fast, for example it took 1–2 min to be completed for the very reactive dinitroarenes **16** and **17**. Disappointing yields for some compounds, especially when the VNS was carried out in the *t*-BuOK/DMF system, might be attributed to side reactions like substitution of the benzotriazole residue. From the reaction of **1** and **12** I isolated only the VNS product **12a**, substituted *ortho* to the nitro group. The low yield (7 or 20%) was partly due to tedious purification, which included preparative TLC. But generally the yields were good, even for the less electrophilic heterocycles **18** and **20**. Compared to the bulky sulphonyl group the steric requirements imposed by the sulphoxide group are much lower, so the latter one can adopt considerably easier a favourable conformation for the anti elimination. Small amounts of 1-nitronaphthalene-2-carboxaldehyde (**13b**) were also isolated from the reactions of **13** and **2** in both base/solvent systems.

Finally, I conducted the VNS experiments using sulphones **4**, **7**, **10** and sulphoxides **5**, **8**, **11** (Scheme 6, Table 2). Apart from the reaction of the triazole derivatives with 1,3-dinitrobenzene (**16**) and nitrobenzotriazole **22** the results were usually disappointing. Regardless of the system base/solvent used, only the VNS product **24** was isolated in 16–46% yield from the reaction mixtures of the carbanion precursors **4** or **5** with 1,3-dinitrobenzene (**16**). The carbanion precursor **7** treated with **16** gave both VNS and ONSH products **25a** and **25b** in low yields, regardless of conditions used, whereas the reactions of sulphoxide **8** with **16** led only to compound **25a**. Apart from the difficulties in the elimination step, the low yields of these products may be due to low stability of carbanions derived from sulphones **4**, **7** and sulphoxides **5**, **8** in the strong alkaline medium.

Similar factors like those discussed for the reaction of sulphone **1** or sulphoxide **2** with nitroarenes seem to govern the reaction course in the other sulphones and sulphoxides containing azole rings. Hence, apart from compound **4**, the reactions of sulphones **7** and **10** led to both VNS and ONSH products, while the reactions of sulphoxides **5**, **8** and **11** gave only the VNS products.

In conclusion, the above discussed reactions provide some insight into the elimination process, particularly steric



Scheme 6.

requirements, involving the phenylsulphinate anion as the leaving group in the VNS of hydrogen. Although the SO_2Ar and SOAr groups are common leaving groups in aromatic nucleophilic substitution they are not generally lost in the VNS.[2,3,24] However, the SO_2Ar could be forced to leave on further transformations involving the VNS products.[4,17,23,25–27] Furthermore, the described method afforded compounds with the benzotriazole residue. Taking into account a plethora of possibilities of the exchange of this group for other moieties,[9] the obtained compounds may be useful as starting materials for further synthesis. Some of the products may be also interesting due to their biological properties because diaryl- and dihetarylmethanes are known as effective anti-HIV1 agents.[28]

Table 2. Products of the reaction of sulphones **4**, **7**, **10** or sulphoxides **5**, **8**, **11** with nitroarenes **16**, **18** or **22**

Starting materials	Products	Yields (%)	
		Method A[a]	Method B
4+**16**	**24**	43	46
5+**16**	**24**	32	16
7+**16**	**25a**	18	10
	25b	3	13
8+**16**	**25a**	4	10
10+**16**	**26a**	74	34
	26b	0	29
11+**16**	**26a**	38	37
10+**22**	**27a**	78	46
	27b	0	17
11+**18**	**28**	9	3

[a] Method A: KOH/DMSO/23°C; method B: *t*-BuOK/DMF/−30°C.

Experimental

$MgSO_4$ was used for drying extracts. Flash chromatography (FC) was performed using silica gel 60, 230–400 mesh (Merck). Preparative TLC was carried out on Merck PLC plates (no 5717). Melting points were determined on a Boetius apparatus and are uncorrected. ^{1}H NMR were recorded at 300 MHz on Varian Unity 300 or Varian Gemini 300 instruments in DMSO-d_6. Low and high resolution mass spectra were run on an AMD 402 instrument. IR spectra were run in KBr on a Specord 75-IR apparatus.

Starting materials, apart from these prepared below were obtained by known procedures[7,23,27,29] or were commercially available.

Abbreviations: sBn=substituted benzyl, Bt=benzotriazole, FC=flash chromatography, SM=starting material.

Lithiation of 1 and subsequent reactions with electrophiles: synthesis of 1a–1b. General method

n-BuLi (1.9 cm^3 of 1.6 mol solution in THF, 3 mmol) was added dropwise to a cooled (−50°C) and stirred solution of benzotriazole **1** (0.82 g, 3 mmol) in dry THF (80 cm^3). Stirring was continued at this temperature for 20 min and a solution of electrophile (3 mmol) in THF (3 cm^3) was added dropwise. The resulted mixture was stirred for 3 h at −50°C, then the temperature was allowed to rise slowly (2 h) to −10°C, and the reaction mixture was quenched with saturated NH_4Cl (50 cm^3). The organic layer was separated, dried and the solvent was distilled off. The residue was crystallized from EtOH.

1-[Chloro(phenylsulphonyl)methyl]benzotriazole (1a). Yield: 69%. Pale yellow cubes, mp 176–178°C. ^{1}H NMR, δ: 7.54 (ddd, J=8.5, 7 and 1 Hz, 1H, Bt), 7.58–7.82 (m, 6H, Bt+Ph), 7.98–8.01 (m, 1H, Bt), 8.14–8.17 (m, 1H, Bt), 8.98 (s, 1H, CH). IR: 3088, 2968, 1615, 1456, 1341, 1330, 1322, 1287, 1169, 1158, 1034, 815, 771, 757, 730, 715, 688 cm^{-1}. Anal. Calcd for $C_{13}H_{10}ClN_3O_2S$: C 50.73, H 3.28, Cl 11.52, N 13.65; found: C 51.09, H 3.61, Cl 11.48, N 13.91.

1-[Phenylsulphonyl(phenylthio)methyl]benzotriazole (1b). Yield: 48%. Colourless needles, mp 127–129°C. ^{1}H NMR, δ: 7.26–7.72 (m, 12H, Bt+Ph), 8.03–8.07 (m, 2H, Bt), 8.28 (s, 1H, CH). IR: 3055, 2965, 1462, 1449, 1325, 1296, 1168, 1149, 1087, 1039, 748, 720, 696 cm^{-1}. Anal. Calcd for $C_{19}H_{15}N_3O_2S_2$: C 59.82, H 3.96, N 11.02; found: C 59.94, H 4.11, N 11.08.

3,5-Dimethyl-1-(phenylthiomethyl)pyrazole (3). Sodium hydride (0.72 g, 30 mmol) was added portionwise under argon to a stirred solution of 3,5-dimethylpyrazole (2.88 g, 30 mmol) in dry DMF (30 cm^3). The resulted mixture was stirred under argon at 22°C for 30 min and chloromethyl phenyl sulphide (4.92 g, 31 mmol) was added dropwise (the temperature was kept below 50°C). The mixture was stirred under argon at 22°C for 1 h, then at 50°C for 2 h, poured into water (600 cm^3) and extracted with diethyl ether (3×100 cm^3). The combined ethereal extracts were washed with water and dried. The residue after evaporation of the solvent was flash-chromatographed (hexanes–ethyl acetate 1:1) to give 2.95 g (45%) of pyrazole **3** as thick pale yellow oil. The ^{1}H NMR spectrum was in accordance with the published data.[30]

3,5-Dimethyl-1-(phenylsulphonylmethyl)pyrazole (4) and **3,5-dimethyl-1-(phenylsulphinylmethyl)pyrazole (5).** *m*-CPBA (5.18 g, 30 mmol) was added portionwise to a stirred and cooled (0–4°C) solution of compound **3** (2.80 g, 12.8 mmol) in $CHCl_3$ (150 cm^3). Stirring was continued for 5 h at 22°C, the reaction mixture was washed with saturated $NaHCO_3$ (3×40 cm^3) followed by water, and dried. The residue after evaporation of the solvent was flash-chromatographed (ethyl acetate) to give 1.05 g (33%) of pyrazole **4** (R_f=0.75) as colourless needles (60% EtOH), mp 94–96°C, and 1.52 g (50%) of pyrazole **5** (R_f=0.48) as colourless needles (hexanes–ethyl acetate 1:1), mp 80–81°C (lit.[30] 75–76°C). Compound **5** can be also obtained in 66% yield by oxidation of pyrazole **3** with $NaIO_4$ according to a method described for compound **2**.[7] **4**: ^{1}H NMR, δ: 1.95 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 5.70 (s, 2H, CH_2), 5.86 (s, 1H, 4-H), 7.58–7.79 (m, 5H, Ph). IR: 3060, 2975, 2911, 1559, 1445, 1388, 1315, 1296, 1136, 1076, 782, 772, 739, 680 cm^{-1}. Anal. Calcd for $C_{12}H_{14}N_2O_2S$: C 57.58, H 5.64, N 11.19; found: C 57.71, H 5.49, N 11.31.

1-(Phenylsulphonylmethyl)benzimidazole (7) and **1-(phenylsulphinylmethyl)benzimidazole (8).** When 1-(phenylthiomethyl)benzimidazole[8] (**6**) was oxidized with *m*-CPBA according to a known procedure[8] two compounds were detected in the reaction mixture. Separation by FC (ethyl acetate) gave 1.28 g (47%) of sulphone **7** (R_f=0.42) as colourless prisms (benzene), mp 164–165°C (lit.[8] 148–150°C) and 1.08 g (42%) of sulphoxide **8** (R_f=0.12) as colourless prisms (benzene), mp 141–143°C (lit.[8] 138–139°C). The ^{1}H NMR spectra of compounds **7** and **8** were in accordance with the published data.[8]

1-(Phenylthiomethyl)-1,2,4-triazole (9). Compound **9** was obtained from 1,2,4-triazole and chloromethyl phenyl sulfide in an identical manner to that described for compound **3**. Yield: 2.68 g (49%), almost colourless oil. ^{1}H NMR, δ: 5.77 (s, 2H, CH_2), 7.30–7.44 (m, 5H, Ph), 8.00 (s, 1H, 3-H), 8.40 (s, 1H, 5-H). IR: 3105, 3052, 2990, 1504, 1486, 1440, 1276, 1199, 1133, 1011, 752, 690, 675 cm^{-1}. Anal. Calcd for $C_9H_9N_3S$: C 56.52, H 4.74, N 21.97; found: C 56.18, H 4.63, N 22.34.

1-(Phenylsulphonylmethyl)-1,2,4-triazole (10). Compound **9** (3.82 g, 20 mmol) was oxidized with *m*-CPBA (12.40 g, 50 mmol) in a similar manner to that described for compounds **4** and **5**. FC (hexanes–ethyl acetate 1:2) gave 2.48 g (56%) of sulphone **10** as colourless prisms (50% EtOH), mp 166–167°C. ^{1}H NMR, δ: 6.12 (s, 2H, CH_2), 7.62–7.82 (m, 5H, Ph), 8.00 (s, 1H, 3-H), 8.49 (s, 1H, 5-H). IR: 3099, 2966, 2915, 1510, 1446, 1364, 1327, 1297, 1275, 1159, 1133, 1123, 1080, 1000, 779, 761, 686, 675, 641 cm^{-1}. Anal. Calcd for $C_9H_9N_3O_2S$: C 48.42, H 4.06, N 18.82; found: C 48.28, H 4.35, N 18.50.

1-(Phenylsulphinylmethyl)-1,2,4-triazole (11). Compound **9** (1.66 g, 8.7 mmol) was oxidized with $NaIO_4$ (2.82 g, 13.2 mmol) in a similar manner to that described for compound **2**.[7] FC of the crude reaction mixture (hexanes–ethyl acetate 1:2) afforded 1.00 g (56%) of sulphoxide **11** as colourless plates, mp 126–128°C. ^{1}H NMR, δ: 5.50 (d, J=13 Hz, 1H, CH_2), 5.71 (d, J=13 Hz, 1H, CH_2), 7.53–7.63 (m, 5H, Ph), 8.01 (s, 1H, 3-H), 8.40 (s, 1H, 5-H). IR: 3126, 3111, 2994, 2932, 1510, 1452, 1280, 1209, 1129, 1088, 1040, 1016, 769, 740, 697, 672 cm^{-1}. Anal. Calcd for $C_9H_9N_3OS$: C 52.16, H 4.38, N 20.28; found: C 52.38, H 4.37, N 20.44.

Reactions of nitroarenes with sulphones 1, 4, 7, 10 and sulphoxides 2, 5, 8, 11

Method A. Finely powdered KOH (400 mg) was added in one portion to a stirred solution of sulphone (1 mmol) or sulphoxide (1 mmol) and nitroarene (1 mmol) in dry DMSO (5 cm^3) under argon. The resulting dark coloured mixture was vigorously stirred under argon for 20 min at 22°C (if the reaction time was different from 20 min it was given in Table 1), quenched with 3% HCl (30 cm^3) and extracted with $CHCl_3$ (3×20 cm^3). The extract was washed with water, dried and the solvent was removed under vacuum. Further purification procedures are given at the description of individual compounds.

Method B. A solution of sulphone (1 mmol) or sulphoxide (1 mmol) and nitroarene (1 mmol) in dry DMF (4 cm^3) was added to a stirred solution of *t*-BuOK (336 mg, 3 mmol) in dry DMF (3 cm^3). The resulted mixture was stirred for 25 (the reaction of compounds **13**–**15**, **19** and **21**–**23** with sulphoxide **1**) or 90 min at −30°C (if the reaction time was different from these values it was given in Table 1), quenched with 3% HCl (30 cm^3) and extracted with $CHCl_3$ (3×20 cm^3). The extract was washed with water, dried and the solvent was removed under vacuum. Further purification

procedures are given at the description of individual compounds.

Method C. Like method A, but *t*-BuOK (336 mg, 3 mmol) was used instead of KOH.

Method D. Like method B, but oxygen was passed through the reaction mixture.

Method E. A solution of sulphone **1** (273 mg, 1 mmol) or sulphoxide **1** (257 mg, 1 mmol) and nitroarene (1 mmol) in dry THF (7 cm^3) was added dropwise to a solution of *t*-BuOK (336 mg, 3 mmol) in dry THF (3 cm^3). The reaction was carried out as for method B.

Unless otherwise stated, the purification procedure for the particular compound applies to each starting material and method of synthesis.

1-(2-Nitrobenzyl)benzotriazole (12a). Sulphoxide **2** as SM. FC (hexanes–ethyl acetate 2:1, R_f=0.42) followed by preparative TLC (hexanes–ethyl acetate 2:1) and crystallization (70% EtOH). Almost colourless plates, mp 138–139°C. ^{1}H NMR, δ: 6.35 (s, 2H, CH_2), 6.81–6.84 (m, 1H, 6-H Ph), 7.44 and 7.56 (2×ddd, J=8.5, 7 and 1 Hz, 2×1H, Bt), 7.59–7.70 (m, 2H, 4- and 5-H Ph), 7.84–7.87 and 8.09–8.13 (2×m, 2×1H, Bt), 8.19 (dd, J=8 and 1.5 Hz, 1H, 3-H Ph). IR: 3031, 2999, 1500, 1334, 1311, 1289, 1278, 1239, 1206, 1069, 835, 762, 716, 699 cm^{-1}. Anal. Calcd for $C_{13}H_{10}N_4O_2$: C 61.41, H 3.96, N 22.04; found: C 61.30, H 4.17, N 22.41.

1-[2-Nitrophenyl(phenylsulphonyl)methyl]benzotriazole (12b). Sulphone **1** as SM. FC (hexanes–ethyl acetate 2:1, R_f=0.34). Long yellow plates (MeOH), mp 179–181°C. ^{1}H NMR, δ: 7.36–7.47 (m, 5H, Ph+Bt), 7.61–7.66 (m, 3H, Ph+Bt), 7.85 (ddd, J=8.5, 7 and 1 Hz, 1H, Bt), 8.01–8.14 (m, 3H, Ph+Bt), 8.12 (singlet overlapped with multiplet, 1H, CH), 8.86 (dd, J=8 and 1 Hz, 1H, $PhNO_2$). MS, *m/z* (relative intensity, ion): 395 (0.2%, M+H), 253 (100%, M−$PhSO_2$). IR: 3044, 2945, 1530, 1447, 1349, 1330, 1314, 1150, 1049, 742, 721 cm^{-1}. Anal. Calcd for $C_{19}H_{14}N_4O_4S$: C 57.86, H 3.58, N 14.21; found: C 57.94, H 3.34, N 14.39.

1-[4-Nitrophenyl(phenylsulphonyl)methyl]benzotriazole (12c). 4-Fluoronitrobenzene **14** as SM. Method A: crystallization (butanone), method B: FC (hexanes–ethyl acetate 2:1, R_f=0.28) followed by crystallization (butanone). Pale yellow prisms, mp 233–234°C (dec.). ^{1}H NMR, δ: 7.37–7.65 (m, 7H, Bt+Ph), 7.88–7.91 (m, 1H, Bt), 8.05–8.08 (m, 1H, Bt), 8.24 (s, 1H, CH), 8.32–8.36 (m, 2H, 2-H and 6-H sBn), 8.40–8.44 (m, 2H, 3-H and 5-H sBn). IR: 3080, 1518, 1489, 1446, 1347, 1333, 1310, 1294, 1146, 1135, 1060, 748, 739, 686 cm^{-1}. Anal. Calcd for $C_{19}H_{14}N_4O_4S$: C 57.86, H 3.58, N 14.21; found: C 57.75, H 3.93, N 14.44.

1-(1-Nitronaphthalen-2-ylmethyl)benzotriazole (13a). FC (hexanes–ethyl acetate 5:1, R_f=0.30). Yellow prisms (80% EtOH), mp 141–143°C. ^{1}H NMR, δ: 6.24 (s, 2H, CH_2), 7.43 (ddd, J=8.5, 7 and 1 Hz, 1H, Bt), 7.42 (d, J=8.6 Hz, 1H, 3-H naphthalene), 7.58 (ddd, J=8.5, 7 and 1 Hz, 1H, Bt), 7.71–7.83 (m, 4H, Bt+naphthalene), 8.09–8.13 (m, 2H, Bt+naphthalene), 8.21 (d, J=8.6 Hz, 1H, 4-H naphthalene). IR: 3050, 1522, 1511, 1446, 1365, 1340, 1152, 1079, 830, 772, 749 cm^{-1}. Anal. Calcd for $C_{17}H_{12}N_4O_2$: C 67.10, H 3.98, N 18.41; found: C 67.37, H 4.28, N 18.43.

1-Nitro-2-naphthalenecarboxaldehyde (13b). Purification: see **13a**, R_f=0.39. Yellow needles, mp 102–103°C (lit.[18] 100–101°C). ^{1}H NMR, δ: 7.84–7.92 (m, 3H, naphthalene), 8.13 (d, J=8.5 Hz, 1H, 4-H naphthalene), 8.22–8.27 (m, 1H, naphthalene), 8.45 (d, J=8.5 Hz, 1H, 5-H naphthalene), 10.17 (s, 1H, CHO). IR: 1692, 1511, 1502, 1355, 1210, 1046, 821, 763 cm^{-1}. HRMS. Calcd for $C_{11}H_7NO_3$: 201.0426; found: 201.0432.

1-(5-Fluoro-2-nitrobenzyl)benzotriazole (14a). Method B: FC (hexanes–ethyl acetate 2:1, R_f=0.58). Pale yellow prisms (80% EtOH), mp 114–115°C. ^{1}H NMR, δ: 6.36 (s, 2H, CH_2), 6.69 (dd, J_{HF}=9.5 Hz, J_{HH}=2.5 Hz, 1H, 6-H sBn), 7.44–7.62 (m, 3H, 4-H sBn+Bt), 7.89–7.92 and 8.11–8.14 (2×m, 2×1H, Bt), 8.33 (dd, J_{HH}=9 Hz, J_{HF}=5 Hz, 1H, 3-H sBn). IR: 3080, 2915, 1516, 1513, 1488, 1443, 1340, 1326, 1308, 1293, 1142, 1128, 1056, 741, 725, 683 cm^{-1}. Anal. Calcd for $C_{13}H_9FN_4O_2$: C 57.36, H 3.33, N 20.52; found: C 57.17, H 3.58, N 20.59.

1-[5-Fluoro-2-nitrophenyl(phenylsulphonyl)methyl]benzotriazole (14b). Purification: see **14a**, R_f=0.45. Tiny yellow prisms (EtOH), mp 198–200°C (dec.). ^{1}H NMR, δ: 7.34–7.47 (m, 5H, Ph+Bt), 7.61–7.68 (m, 3H, Ph+Bt), 7.78 (ddd, J_{HH}=9 and 3 Hz, J_{HF}=7.5 Hz, 1H, 4-H sBn), 8.07–8.10 (m, 1H, Bt), 8.19 (s, 1H, CH), 8.28 (dd, J_{HH}=9 Hz, J_{HF}=5.5 Hz, 1H, 3-H sBn), 8.59 (dd, J_{HH}=3 Hz, J_{HF}=10 Hz, 1H, 6-H sBn). IR: 3061, 3032, 2975, 1562, 1498, 1425, 1317, 1304, 1291, 1280, 1248, 1123, 1025, 824, 713, 695 cm^{-1}. Anal. Calcd for $C_{19}H_{13}FN_4O_4S$: C 55.34, H 3.18, N 13.59; found: C 55.51, H 3.10, N 13.56.

1-(5-Chloro-2-nitrobenzyl)benzotriazole (15a). FC (hexanes–ethyl acetate 5:1, R_f=0.62). Yellow needles (EtOH), mp 168–169°C. ^{1}H NMR, δ: 6.24 (s, 2H, CH_2), 7.00 (d, J=2.5 Hz, 1H, 6-H sBn), 7.46 and 7.60 (2×ddd, J=8.5, 7 and 1 Hz, 2×1H, Bt), 7.74 (dd, J=9 and 2.5 Hz, 1H, 4-H sBn), 7.90–7.93 (m, 1H, Bt), 8.10–8.14 (m, 1H, Bt), 8.24 (d, J=9 Hz, 1H, 3-H sBn). IR: 3068, 3050, 1609, 1571, 1530, 1524, 1340, 1272, 1096, 895, 846, 748 cm^{-1}. Anal. Calcd for $C_{13}H_9ClN_4O_2$: C 54.09, H 3.14, Cl 12.28, N 19.41; found: C 53.94, H 3.08, Cl 12.33, N 19.51.

1-[5-Chloro-2-nitrophenyl(phenylsulphonyl)methyl]-benzotriazole (15b). Purification: see **15a**, R_f=0.49. Pale yellow needles (EtOH), mp 193–195°C. ^{1}H NMR, δ: 7.32–7.47 (m, 5H, Bt+Ph), 7.60–7.66 (m, 3H, Bt+Ph), 7.99 (dd, J=9 and 2.5 Hz, 1H, 4-H sBn), 8.07–8.10 (m, 1H, Bt), 8.17 (s, 1H, CH), 8.20 (d, J=9 Hz, 1H, 3-H sBn), 8.84 (d, J=2.5 Hz, 1H, 6-H sBn). MS, *m/z* (relative intensity, ion): 429 (0.3%, M+H), 287 (100%, M−$PhSO_2$). IR: 3055, 3010, 1569, 1531, 1451, 1342, 1318, 1305, 1158, 1046, 909, 746, 715, 690 cm^{-1}. Anal. Calcd for $C_{19}H_{13}ClN_4O_4S$: C 53.21, H 3.06, Cl 7.48, N 13.06; found: C 53.46, H 3.06, Cl 7.61, N 13.05.

1-(2,4-Dinitrobenzyl)benzotriazole (16a). Method A (SM:

1): crystallization, method A (SM: **2**) and method B: FC (hexanes–ethyl acetate 2:1, R_f=0.44). Long pale yellow plates (EtOH), mp 155.5–156.5°C. ^{1}H NMR, δ: 6.51 (s, 2H, CH_2), 6.96 (d, J=8.5 Hz, 1H, 6-H sBn), 7.49 and 7.58 (2×ddd, J=8.5, 7 and 1 Hz, 2×1H, Bt), 7.89–7.92 and 8.12–8.15 (2×m, 2×1H, Bt), 8.46 (dd, J=8.5 and 2.5 Hz, 1H, 5-H sBn), 8.88 (d, J=2.5 Hz, 1H, 3-H sBn). IR: 3097, 3066, 3051, 3040, 1586, 1575, 1521, 1490, 1472, 1325, 1289, 1242, 1205, 1126, 1073, 1036, 814, 774, 766, 718, 704 cm^{-1}. Anal. Calcd for $C_{13}H_9N_5O_4$: C 52.18, H 3.03, N 23.41; found: C 52.14, H 3.15, N 23.29.

1-[2,4-Dinitrophenyl(phenylsulphonyl)methyl]benzotriazole (16b). Purification: see **16a**, method B, R_f=0.40. Yellow–orange needles (EtOH), mp 205–206°C. ^{1}H NMR, δ: 7.28–7.31 (m, 1H, Bt), 7.37–7.48 (m, 4H, Bt+Ph). 7.61–7.70 (m, 3H, Bt+Ph), 8.07–8.10 (m, 1H, Bt), 8.25 (s, 1H, CH), 8.81 (d, J=2.5 Hz, 1H, 3-H sBn), 8.88 (dd, J=9 and 2.5 Hz, 1H, 5-H sBn), 9.16 (d, J=9 Hz, 1H, 6-H sBn). IR: 3092, 3040, 2980, 1534, 1445, 1349, 1334, 1303, 1146, 1037, 748, 732, 711 cm^{-1}. Anal. Calcd for $C_{19}H_{13}N_5O_6S$: C 51.93, H 2.98, N 15.94; found: C 51.88, H 3.05, N 16.27.

1-(5-Chloro-2,4-dinitrobenzyl)benzotriazole (17a). FC (hexanes–ethyl acetate 2:1, R_f=0.53). Yellow plates (EtOH), mp 133–134°C. ^{1}H NMR, δ: 6.41 (s, 2H, CH_2), 7.32 (s, 1H, 6-H sBn), 7.48 and 7.62 (2×ddd, J=8.5, 7 and 1 Hz, 2×1H, Bt), 7.92–7.95 and 8.11–8.14 (2×m, 2×1H, Bt), 8.96 (s, 1H, 3-H sBn). IR: 3090, 1619, 1588, 1535, 1348, 1325, 1273, 1166, 1095, 962, 836, 754 cm^{-1}. Anal. Calcd for $C_{13}H_8ClN_5O_4$: C 46.79, H 2.42, Cl 10.62, N 20.99; found: C 47.02, H 2.55, Cl 10.59, N 20.84.

1-[5-Chloro-2,4-dinitrophenyl(phenylsulphonyl)methyl]benzotriazole (17b). Purification: see **17a**, R_f=0.49. Yellow needles (EtOH), mp 165–167°C. ^{1}H NMR, δ: 7.25–7.28 (m, 1H, Bt), 7.37–7.49 (m, 4H, Bt+Ph), 7.60–7.71 (m, 3H, Bt+Ph), 8.08–8.11 (m, 1H, Bt), 8.27 (s, 1H, CH), 8.96 (s, 1H, 3-H), 9.07 (s, 1H, 6-H). IR: 3095, 3044, 1599, 1581, 1546, 1534, 1451, 1342, 1320, 1153, 1045, 835, 741, 716, 683 cm^{-1}. Anal. Calcd for $C_{19}H_{12}ClN_5O_6S$: C 48.66, H 2.55, Cl 7.48, N 14.78; found: C 48.87, H 2.77, Cl 7.31, N 14.90.

1-(2,4-Dinitro-5-phenylsulphonylbenzyl)benzotriazole (17c). Purification: see **17a**, R_f=0.27. Pale yellow needles (EtOH), mp 183–186°C. ^{1}H NMR, δ: 6.48 (s, 2H, CH_2), 7.52 (ddd, J=8.5, 7 and 1 Hz, 1H, Bt), 7.52 (s, 1H, 6-H sBn), 7.59–7.65 (m, 5H, Bt+Ph), 7.75–7.80 (m, 1H, Ph), 7.83–7.86 and 8.17–8.20 (2×m, 2×1H, Bt), 8.95 (s, 1H, 3-H sBn). IR: 3088, 3064, 3034, 2977, 1543, 1367, 1352, 1327, 1155, 840, 830, 757, 747, 725, 602 cm^{-1}. Anal. Calcd for $C_{19}H_{13}N_5O_6S$: C 51.93, H 2.98, N 15.94; found: C 51.65, H 2.82, N 15.55.

1-(1-Methyl-4-nitropyrazol-5-ylmethyl)benzotriazole (18a). Sulphoxide **2** as SM. FC (hexanes–ethyl acetate 1:1, R_f=0.36). Almost colourless prisms (MeOH), mp 146–147°C. ^{1}H NMR, δ: 4.08 (s, 3H, CH_3), 6.38 (s, 2H, CH_2), 7.45 and 7.65 (2×ddd, J=8.5, 7 and 1 Hz, 2×1H, Bt), 7.93–7.97 and 8.07–8.10 (2×m, 2×1H, Bt), 8.38 (s, 1H, 3-H). IR: 3113, 2994, 1560, 1501, 1456, 1440, 1408, 1376, 1318, 1304, 1291, 1229, 1190, 1158, 1134, 1093, 929, 829, 777, 762 cm^{-1}. Anal. Calc. for $C_{11}H_{10}N_6O_2$: C 51.16, H 3.90, N 32.55; found: C 51.09, H 4.12, N 32.56.

1-[1-Methyl-4-nitropyrazol-5-yl(phenylsulphonyl)methyl]benzotriazole (18b). Sulphone **1** as SM. Purification: see **18a**, R_f=0.49. Green–yellow prisms (MeOH), mp 195–196°C. ^{1}H NMR, δ: 4.41 (s, 3H, CH_3), 7.22–7.26 (m, 1H, Bt), 7.46–7.64 (m, 4H, Bt+Ph), 7.79–7.88 (m, 3H, Ph), 8.16–8.19 (m, 1H, Bt), 8.48 (s, 1H, 3-H pyrazole or CH), 8.52 (s, 1H, 3-H pyrazole or CH). IR: 3088, 3061, 2962, 1515, 1459, 1414, 1380, 1353, 1341, 1321, 1157, 1063, 772, 755, 724 cm^{-1}. Anal. Calcd for $C_{17}H_{15}N_6O_4S$: C 51.12, H 3.79, N 21.04; found: C 51.23, H 3.58, N 21.09.

1-[3-Methyl-4-nitro-1-(4-nitrophenyl)-pyrazol-5-ylmethyl]benzotriazole (19a). FC (hexanes–ethyl acetate 2:1, R_f=0.34). Yellow plates (EtOH), mp 194–195°C. ^{1}H NMR, δ: 2.58 (s, 3H, CH_3), 6.32 (s, 2H, CH_2), 7.40 and 7.57 (2×ddd, J=8.5, 7 and 1 Hz, 2×1H, Bt), 7.78–7.81 (m, 1H, Bt), 7.85–7.90 (m, 2H, Ph), 7.98–8.01 (m, 1H, Bt), 8.28–8.33 (m, 2H, Ph). IR: 3089, 1574, 1525, 1501, 1446, 1349, 865, 826, 751 cm^{-1}. Anal. Calcd for $C_{17}H_{13}N_7O_4$: C 53.82, H 3.45, N 25.85; found: C 53.91, H 3.40, N 26.14.

1-[3-Methyl-4-nitro-1-(4-nitrophenyl)pyrazol-5-yl(phenylsulphonyl)methyl]benzotriazole (19b). FC (hexanes–ethyl acetate 1:1, R_f=0.55). Long yellow plates (EtOH), mp 188–190°C (dec.). ^{1}H NMR, δ: 2.54 (s, 3H, CH_3), 7.09–7.12 (m, 1H, Bt), 7.38–7.61 (m, 6H, Bt+Ph+4-nitrophenyl), 7.76–7.82 (m, 3H, Bt+Ph), 8.01–8.04 (m, 1H, Bt), 8.17–8.22 (m, 2H, 4-nitrophenyl), 8.51 (s, 1H, CH). IR: 3071, 2927, 1552, 1520, 1502, 1450, 1155, 760, 751, 686 cm^{-1}. Anal. Calcd for $C_{23}H_{17}N_7O_6S$: C 53.18, H 3.30, N 18.87; found: C 52.90, H 3.49, N 18.75.

1-(1-ethyl-2-methyl-4-nitroimidazol-5-yl)methylbenzotriazole (20a). FC (hexanes–ethyl acetate 1:1, R_f=0.09). Colourless plates (70% MeOH), mp 142–144°C. ^{1}H NMR, δ: 1.05 (t, J=7.5 Hz, 3H, CH_2CH_3), 2.44 (s, 3H, N-CH_3), 4.25 (q, J=7.5 Hz, 2H, CH_2CH_3), 6.34 (s, 2H, Ar-CH_2), 7.45 and 7.63 (2×ddd, J=8.5, 7 and 1 Hz, 2×1H, Bt), 7.87–7.90 and 8.06–8.10 (2×m, 2×1H, Bt). IR: 3050, 2990, 2969, 2930, 1572, 1539, 1514, 1458, 1431, 1420, 1393, 1356, 1336, 1293, 781, 745 cm^{-1}. Anal. Calcd for $C_{13}H_{14}N_3O_2$: C 68.40, H 6.18, N 18.41; found: C 68.29, H 6.06, N 18.66.

1-(1-Ethyl-5-nitroindazol-4-ylmethyl)benzotriazole (21a). FC (hexanes–ethyl acetate 1:1, R_f=0.23). Yellow needles (EtOH), mp 149–150°C. ^{1}H NMR, δ: 1.50 (t, J=7 Hz, 3H, CH_3), 4.52 (q, J=7 Hz, 2H, CH_2), 6.48 (s, 2H, CH_2Ar), 7.43 and 7.58 (2×ddd, J=8.5, 7 and 1 Hz, 2×1H, Bt), 7.82–7.85 (m, 1H, Bt), 7.87 (d, J=9.5 Hz, 1H, 7-H), 7.95 (d, J=9.5 Hz, 1H, 6-H), 8.05–8.08 (m, 1H, Bt), 8.73 (s, 1H, 4-H). IR: 3142, 3109, 3032, 2989, 2977, 1618, 1519, 1467, 1352, 1340, 1321, 1298, 1239, 1091, 830, 756 cm^{-1}. Anal. Calcd for $C_{16}H_{14}N_6O_2$: C 59.62, H 4.38, N 26.07; found: C 59.60, H 4.29, N 26.25.

1-(2-Methyl-5-nitrobenzotriazol-4-ylmethyl)benzotriazole (22a). Method A: crystallization, method B: FC (hexanes–ethyl acetate 1:1, R_f=0.37). Pale yellow needles (EtOH), mp 182–183°C. ^{1}H NMR, δ: 4.55 (s, 3H, CH_3), 6.55 (s, 2H,

CH_2), 7.42 and 7.59 (2×ddd, J=8.5, 7 and 1 Hz, 2×1H, Bt), 7.90–7.93 and 8.03–8.06 (2×m, 2×1H, Bt), 8.12 (d, J=9.5 Hz, 1H, 7-H Bt), 8.24 (d, J=9.5 Hz, 1H, 6-H Bt). IR: 3079, 2940, 1609, 1527, 1444, 1347, 1336, 1288, 839, 825, 785, 754, 741, 731 cm^{-1}. Anal. Calcd for $C_{14}H_{11}N_7O_2$: C 54.36, H 3.59, N 31.70; found: C 54.42, H 3.90, N 31.56.

1-[2-Methyl-5-nitrobenzotriazol-4-yl(phenylsulphonyl)-methyl]benzotriazole (22b). Purification: see **22a**, method B, R_f=0.30. Pale yellow needles (EtOH), mp 183–185°C. ^1H NMR, δ: 4.31 (s, 3H, CH_3), 7.40–7.53 (m, 5H, Bt+Ph), 7.67–7.73 (m, 3H, Bt+Ph), 8.10–8.13 (m, 1H, Bt), 8.12 (d, J=9.5 Hz, 1H, 7-H Bt), 8.35 (d, J=9.5 Hz, 1H, 6-H Bt), 8.56 (s, 1H, CH). IR: 3085, 3050, 2950, 1529, 1450, 1344, 1156, 1052, 771, 752, 739 cm^{-1}. Anal. Calcd for $C_{20}H_{15}N_7O_4S$: C 53.44, H 3.36, N 21.82; found: C 53.47, H 3.64, N 21.89.

5-(Benzotriazol-1-ylmethyl)-6-nitroquinoline (23a). FC (hexanes–ethyl acetate 1:1, R_f=0.35). Pale yellow needles (EtOH), mp 174–176°C. ^1H NMR, δ: 6.55 (s, 2H, CH_2), 7.44 and 7.62 (2×ddd, J=8.5, 7 and 1 Hz, 2×1H, Bt), 7.78–7.82 (m, 1H, 3-H quinoline), 7.90–7.93 (m, 1H, Bt), 8.04–8.07 (m, 1H, Bt), 8.33 (d, J=9.5 Hz, 1H, 7-H or 8-H quinoline), 8.36 (d, J=9.5 Hz, 1H, 7-H or 8-H quinoline), 8.99 (dd, J=9 and 1 Hz, 1H, 4-H quinoline), 9.15 (dd, J=4 and 1 Hz, 1H, 2-H quinoline). IR: 3099–3030, 1597, 1516, 1492, 1468, 1338, 1318, 1080, 846, 831, 775, 743 cm^{-1}. Anal. Calcd for $C_{16}H_{11}N_5O_2$: C 62.94, H 3.63, N 22.94; found: C 62.96, H 3.75, N 22.64.

5-[Benzotriazol-1-yl(phenylsulphonyl)methyl]-6-nitro-quinoline (23b). Purification: see **23a**, R_f=0.29. Colourless needles (EtOH), mp 197–198°C. ^1H NMR, δ: 7.17–7.20 (m, 1H, Bt), 7.41–7.52 (m, 2H, Bt), 7.55–7.60 (m, 2H, Ph+Bt), 7.74–7.87 (m, 4H, Ph+quinoline), 8.13–8.16 (m, 1H, Bt), 8.32 (d, J=9 Hz, 1H, 7-H quinoline), 8.33 (s, 1H, CH), 8.45 (d, J=9 Hz, 1H, 8-H quinoline), 9.12 (dd, J=4 and 1.5 Hz, 1H, 2-H quinoline), 9.34 (dd, J=8.5 and 1 Hz, 1H, 4-H quinoline). IR: 3056, 2972, 2915, 1494, 1457, 1449, 1333, 1318, 1291, 1227, 1154, 1085, 1068, 931, 890, 786, 773, 765, 738, 686 cm^{-1}. Anal. Calcd for $C_{22}H_{15}N_5O_4S$: C 59.32, H 3.39, N 15.72; found: C 59.48, H 3.51, N 15.61.

3,5-Dimethyl-1-(2,4-dinitrobenzyl)pyrazole (24). FC (hexanes–ethyl acetate 2:1, R_f=0.40). Pale yellow prisms (50% EtOH), mp 104–106°C. ^1H NMR, δ: 2.11 (s, 3H, CH_3), 2.16 (s, 3H, CH_3), 5.69 (s, 2H, CH_2), 5.97 (s, 1H, 4-H pyrazole), 6.75 (d, J=8.5 Hz, 1H, 6-H sBn), 8.51 (dd, J=8.5 and 2.5 Hz, 1H, 5-H sBn), 8.81 (d, J=2.5 Hz, 1H, 3-H sBn). IR: 3081, 3060–3015, 1604, 1548, 1534, 1453, 1413, 728 cm^{-1}. Anal. Calcd for $C_{12}H_{12}N_4O_4$: C 52.17, H 4.38, N 20.28; found: C 51.93, H 4.20, N 20.33.

1-(2,4-Dinitrobenzyl)benzimidazole (25a). FC (hexanes–ethyl acetate 1:1, R_f=0.29). Cream plates (50% EtOH), mp 166–168°C. ^1H NMR, δ: 6.07 (s, 2H, CH_2), 6.79 (d, J=8.5 Hz, 1H, 6-H sBn), 7.22–7.90 (4×m, 4H, benzimidazole), 8.38 (s, 1H, 2-H benzimidazole), 8.42 (dd, J=8.5 and 2.5 Hz, 1H, 5-H sBn), 8.87 (d, J=2.5 Hz, 1H, 3-H sBn). IR: 3102, 3081, 3051, 2959, 1612, 1601, 1528, 1491, 1480, 1459, 1348, 1270, 744, 740, 730 cm^{-1}. Anal. Calcd for $C_{14}H_{10}N_4O_4$: C 56.38, H 3.38, N 18.79; found: C 56.43, H 3.21, N 18.98.

1-[2,4-Dinitrophenyl(phenylsulphonyl)methyl]benzimi-dazole (25b). Purification: see **25a**, R_f=0.60. Pale yellow cubes (80% EtOH), mp 200–201°C. ^1H NMR, δ: 6.99–7.66 (4×m, 9H, benzimidazole+Ph), 8.51 (s, 1H, 2-H benzimi-dazole), 8.79 (dd, J=8.5 and 2.5 Hz, 1H, 5-H sBn), 8.82 (d, J=2.5 Hz, 1H, 3-H sBn), 9.03 (d, J=8.5 Hz, 1H, 6-H sBn). IR: 3107, 3086, 3054, 1614, 1553, 1539, 1499, 1462, 1352, 1328, 1315, 1275, 1151, 754, 735, 719 cm^{-1}. Anal. Calcd for $C_{20}H_{14}N_4O_6S$: C 54.79, H 3.22, N 12.78; found: C 54.39, H 3.43, N 12.96.

1-(2,4-Dinitrobenzyl)-1,2,4-triazole (26a). FC (hexanes–ethyl acetate 1:2, R_f=0.21). Pale yellow plates (50% EtOH), mp 106–107°C. ^1H NMR, δ: 5.95 (s, 2H, CH_2), 7.30 (d, J=8.5 Hz, 1H, 6-H sBn), 8.10 (s, 1H, 3-H triazole), 8.54 (dd, J=8.5 and 2.5 Hz, 1H, 5-H sBn), 8.81 (d, J=2.5 Hz, 1H, 3-H sBn). IR: 3102, 3089, 2990, 1609, 1530, 1514, 1375, 1353, 1283, 1139, 1015, 842, 781, 732, 685 cm^{-1}. Anal. Calcd for $C_9H_7N_5O_4$: C 43.38, H 2.83, N 28.10; found: C 43.65, H 3.18, N 28.02.

1-[2,4-Dinitrophenyl(phenylsulphonyl)methyl]-1,2,4-tri-azole (26b). Purification: see **26a**, R_f=0.55. Pale yellow needles (50% EtOH), mp 150–152°C. ^1H NMR, δ: 7.59–7.66 (m, 4H, Ph), 7.78–7.84 (m, 1H, Ph), 7.87 (s, 1H, CH), 8.25 (s, 1H, 3-H triazole), 8.75 (dd, J=8.5 and 2.5 Hz, 1H, 5-H sBn), 8.78 (s, 1H, 5-H triazole), 8.82 (d, J=2.5 Hz, 1H, 3-H sBn), 8.91 (d, J=8.5 Hz, 1H, 6-H sBn). IR: 3112, 3056, 2989, 1602, 1537, 1376, 1345, 1309, 1277, 1151, 1130, 837, 738, 716, 642 cm^{-1}. Anal. Calcd for $C_{15}H_{11}N_5O_6S$: C 46.27, H 2.85, N 17.99; found: C 46.20, H 3.12, N 17.98.

2-Methyl-5-nitro-4-(1,2,4-triazol-1-ylmethyl)benzotriazole (27a). Method A: crystallization; method B: FC (hexanes–ethyl acetate 1:2, R_f=0.12). Yellow plates (EtOH), mp 160–161°C. ^1H NMR, δ: 4.61 (s, 3H, CH_3), 6.08 (s, 2H, CH_2), 7.89 (s, 1H, 3-H triazole), 8.08 (d, J=9 Hz, 1H, 7-H Bt), 8.21 (d, J=9 Hz, 1H, 6-H Bt), 8.68 (s, 1H, 5-H triazole). IR: 3119, 3053, 2989, 1534, 1513, 1439, 1367, 1353, 1273, 1141, 1026, 841, 836, 752, 685 cm^{-1}. Anal. Calcd for $C_{10}H_9N_7O_2$: C 46.33, H 3.50, N 37.82; found: C 46.31, H 3.29, N 37.76.

2-Methyl-5-nitro-4-[phenylsulphonyl(1,2,4-triazol-1-yl)-methyl]benzotriazole (27b). Purification: see **27a**, method B, R_f=0.25. Almost colourless prisms (EtOH), mp 192–194°C. ^1H NMR, δ: 4.63 (s, 3H, CH_3), 7.64–7.86 (m, 5H, Ph), 7.97 (s, 1H, 3-H triazole), 8.07 (s, 1H, CH), 8.15 (d, J=9 Hz, 1H, 7-H Bt), 8.44 (d, J=9 Hz, 1H, 6-H Bt), 9.48 (s, 1H, 5-H triazole). IR: 3088, 3010, 1530, 1452, 1348, 1284, 1204, 1157, 1130, 730, 680, 649 cm^{-1}. Anal. Calcd for $C_{16}H_{13}N_7O_4S$: C 48.12, H 3.28, N 24.55; found: C 47.84, H 3.41, N 24.69.

1-(1-Methyl-4-nitropyrazol-5-ylmethyl)-1,2,4-triazole (28). FC (hexanes–ethyl acetate 1:2, R_f=0.11). Pale yellow prisms, mp 146–148°C (MeOH). ^1H NMR, δ: 4.04 (s, 3H, CH_3), 5.88 (s, 2H, CH_2), 8.00 (s, 1H, 3-H triazole), 8.32 (s, 1H, 3-H pyrazole), 8.72 (s, 1H, 5-H triazole). IR: 3116, 3099, 1604, 1501, 1498, 1433, 1406, 1395, 1307, 1122,

750, 673 cm^{-1}. Anal. Calcd for $C_7H_8N_6O_2$: C 40.39, H 3.87, N 40.37; found: C 40.51, H 3.89, N 40.32.

Synthesis of compound 17c from benzotriazole derivative 17a. A solution of benzotriazole derivative **17a** (50 mg, 0.15 mmol) and sodium benzenesulphinate (25 mg, 0.15 mmol) in DMSO (2 cm^3) was stirred at 23°C for 1 h and diluted with water. The precipitated yellow solid was filtered off and crystallized from EtOH to give 44 mg (67%) of compound **17c** as pale yellow needles, mp 182–184°C.

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