Articles

Nitroarylamines via the Vicarious Nucleophilic Substitution of Hydrogen: Amination, Alkylamination, and Arylamination of Nitroarenes with Sulfenamides

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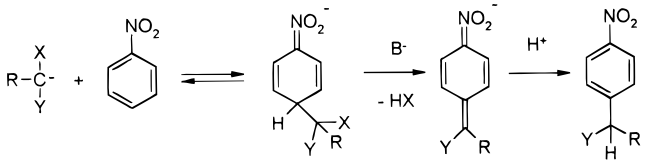
A new reaction of sulfenamides with electrophilic arenes under basic conditions is described. The σ adducts formed from nitroarenes and the anions of sulfenamides undergo elimination of thiol to produce the corresponding *o*- and/or *p*-nitroanilines. This reaction is analogous to the known alkylation and hydroxylation of nitroarenes via the vicarious nucleophilic substitution of hydrogen (VNS). The reaction gives access to a wide range of substituted nitroanilines, nitronaphthylamines, and aminoheterocycles. By means of the reaction with *N*-alkyl- and *N*-arylsulfenamides, it is possible to obtain *N*-alkylnitroanilines and nitrodiarylamines. By varying the structure of sulfenamide and the reaction conditions, particularly the nature and concentration of the base, it is possible to control the orientation of amination.

Introduction

Nitroanilines are important intermediates in organic synthesis and industry, particularly for pharmaceuticals, dyes, and plant protection products. There are many methods for the introduction of amino groups into aromatic rings, among them being the classical S_NAr displacement of halogen which is still of general use.[1] Recently, there has been growing interest in the direct nucleophilic replacement of hydrogen with the amino group in electrophilic arenes.[2] The Chichibabin reaction, replacement of hydride anion in the reaction of electrophilic heterocycles with sodium or potassium amides,[3] was recently substantially improved and extended by use of an external oxidant, $KMnO_4$ in liquid ammonia.[4] This oxidative variant of the Chichibabin reaction is also applicable to some electrophilic nitroarenes. Alternatively, nitroanilines can be obtained via oxidative nucleophilic amination and amidation of nitroarenes with anilines and amides.[5,6]

The vicarious nucleophilic substitution (VNS) reaction offers a great potential for nucleophilic substitution of hydrogen with carbon and oxygen groups.[7,8] This process consists of the addition of nucleophiles containing leaving groups X at the anionic center to nitroarenes followed by base induced β-elimination of HX from the initially formed σ^H adducts (Scheme 1). Nitrophenols can be obtained in this way when nitroarenes are treated with *tert*-butyl or cumyl hydroperoxides in the presence of a base.

Scheme 1



The direct amination of nitroarenes with hydroxylamine in basic media, known for almost 100 years, apparently proceeds along a similar pathway. This reaction is, however, limited to highly electrophilic arenes such as *m*-dinitrobenzene and bicyclic nitroarenes.[9] There are also a few known examples of aminations with hydroxylamine-*O*-sulfonic acid[10] and hydrazine[11] that can be considered as examples of the VNS reaction. Some years ago 4-amino-1,2,4-triazoles were reported to be efficient agents for aminating nitroarenes according to the VNS pathway.[12] Recently short papers describing base-induced amination of nitroarenes with *O*-methyl-

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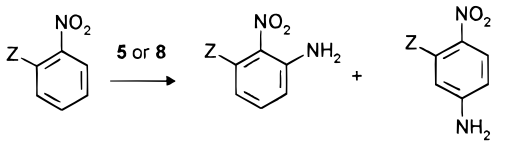
Table 1. Reactions of Sulfenamides 5 and 8 with Nitrobenzene and Its 2-Substituted Derivatives



1, 1a-g **10, 10a-g** **11, 11a-g**

entry	arene	Z	sulfenamide, conditions[a]	products of amination (yield, %)	other products (yield, %)
1	**1**	H	**5**, A	**10** (34), **11** (35)	
2			**8**, A	**10** (14), **11** (71)	
3	**1a**	NO_2	**8**, A		**14** (33), **15** (10)
4	**1b**	CN	**8**, A	**11b** (59)	
5	**1c**	CF_3	**5**, A	**10c** (14), **11c** (33)	
6			**8**, A	**11c** (71)	
7	**1d**	F	**5**, A	**11d** (21)	**10** (53), **16** (8)[b]
8			**8**, A	**11d** (48)	**15** (30)
9			**8**, B		**15** (78)
10	**1e**	Cl	**8**, A	**11e** (72)	
11			**8**, A[c]	**11e** (60)	**15** (23)
12	**1f**	Br	**8**, A	**11f** (66)	
13	**1g**	MeO	**8**, A	**11g** (39)	

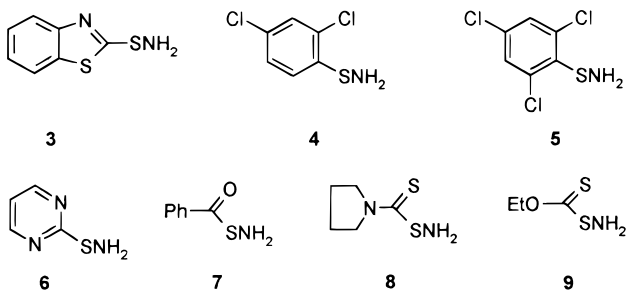
[a] Procedures A, B: see Experimental Section. [b] **16**: 2-(*tert*-Butoxy)nitrobenzene. [c] Procedure A with reversed order of additions.

hydroxylamine in the presence of copper salts[13] and with 1,1,1-trimethylhydrazinium iodide[14] were published.

Taking into account our experience in VNS reactions with carbanions and the wide possibilities connected with this process, we attempted to design efficient and versatile reagents for VNS amination. The reagents should have the general formula NH_2X where X should provide moderate stabilization of a negative charge on the adjacent nitrogen atom, thus facilitating its deprotonation, and simultaneously X should behave as a good leaving group in the base-induced β-elimination. For the VNS reactions of carbanions the reagents contain such leaving groups X as halogens, RS, or RO. Since *N*-haloamines are strong oxidants and are unstable in the presence of bases and whereas *O*-alkylhydroxylamines appear to be insufficiently acidic, we have envisioned sulfenamides $RSNH_2$ as efficient aminating agents. Although simple sulfenamides (R = alkyl, phenyl) are relatively unstable, those containing proper R such as 2-benzothiazyl, 2,4,6-trichlorophenyl, or $Me_2NC(S)$ are sufficiently stable and are readily prepared via simple reactions of the corresponding thiolates with ammonia and sodium hypochlorite.[15] In our preliminary communication we have reported a few examples showing that a variety of sulfenamides are efficient and versatile reagents for aminating nitroarenes.[16] Here we present a full account of our studies on this reaction.

Results and Discussion

Selection of Sulfenamides. To select the most efficient aminating agents, several representative and synthetically available sulfenamides were synthesized.[15] 2-Benzothiazolesulfenamide (**3**), 2,4-dichlorobenzenesulfenamide (**4**), 2,4,6-trichlorobenzenesulfenamide (**5**), 2-pyrimidinesulfenamide (**6**), benzoylsulfenamide (**7**),



N-tetramethylenethiocarbamoylsulfenamide (**8**), and ethoxythiocarbonylsulfenamide (**9**) were subjected to the reaction with nitrobenzene (**1**) and 1-nitronaphthalene (**2**) using two sets of standard VNS conditions:[7] *t*-BuOK/DMF/rt (procedure A) and KOH/DMSO/rt (procedure B). The most satisfactory yields of amination were obtained with sulfenamides **5** and **8**. The former reagent showed a preference for *ortho* substitution, whereas the latter compound reacted at the *para* position of the nitroarene ring. 2-Benzothiazolesulfenamide (**3**) appeared to be a useful reagent for the selective amination of 1-nitronaphthalene, although it was only moderately efficient in the reaction with nitrobenzene.

Nitroarenes. The amination of a variety of substituted nitrobenzenes, nitronaphthalenes, and nitrohet-

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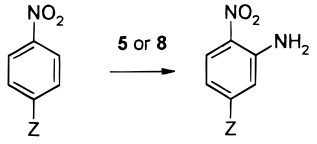
Table 2. Reactions of Sulfenamides 5 and 8 with 4-Substituted Nitrobenzenes



17a-g **18a-g**

entry	arene	Z	sulfenamide, conditions[a]	products of amination (yield, %)	other products (yield %)
1	**17a**	NO_2	**5**, A		**19** (50%), **20** (8%)[b]
2	**17b**	CN	**5**, A	**18b** (32)	**11** (11), **21** (36), **22** (5)
3	**17c**	CF_3	**5**, A	**18c** (35)	
4			**5**, C	**18c** (42)	
5	**17d**	F	**5**, A	**18d** (35)	**11** (31)
6			**5**, A[c]	**18d** (7)	**23** (66)
7			**8**, A		**19** (84)
8	**17e**	Cl	**5**, A	**18e** (60)	
9			**5**, A[c]	**18e** (57)	**23** (15)
10			**8**, A	**18e** (10)	**19** (37)
11			**8**, A[c]	**18e** (4)	**19** (56)
12	**17f**	MeO	**5**, A	**18f** (44)	**11** (29)
13	**17g**	*t*-Bu	**5**, A	**18g** (63)	

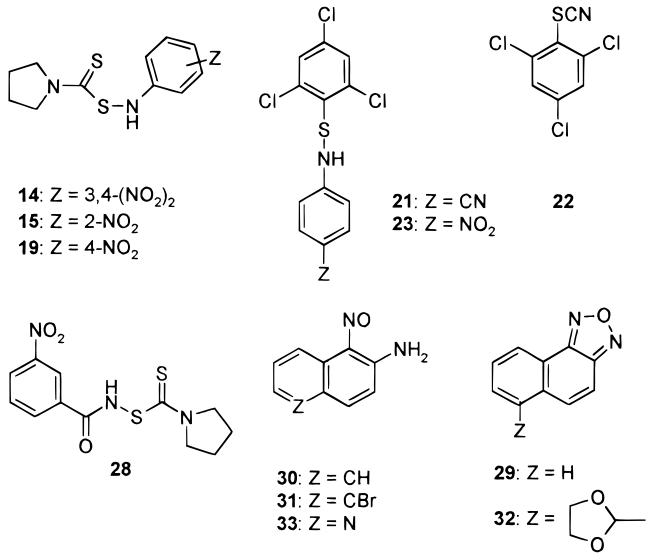
[a] Procedures A, B, C: see Experimental Section. [b] **20**: 4-(*tert*-Butoxy)nitrobenzene. [c] Procedure A with reversed order of additions.

erocycles with **5** and **8** occurred smoothly to give the expected nitroarylamines.

The results of the amination of *ortho*-substituted nitrobenzenes **1a**−**g** with sulfenamides **5** and **8** are presented in Table 1. When **1a**−**g** were reacted with sulfenamide **8** under the conditions of procedure A (*t*-BuOK/DMF), 4-nitroanilines **11a**−**g** were formed exclusively (entries 4, 6, 10, 12, and 13). Substitution at position 6 was possible only with sulfenamide **5** in *o*-nitro(trifluoromethyl)benzene **1c**, yielding a mixture of 4- and 6-aminated products (Table 1, entries 5 and 6). Selective amination of 2-substituted nitroarenes at position 6 was not achieved despite varying the reaction conditions. The yield of the amination of *o*-fluoronitrobenzene (**1d**) with **8** was lower than that in the other cases because of the competing S_NAr substitution of fluorine; nevertheless the VNS reaction was the predominant process (entry 8). The reaction of **5** with fluoronitrobenzene **1d** yielded more S_NAr product (entry 7), perhaps because of the greater tendency of reagent **5** to react at position *ortho*.

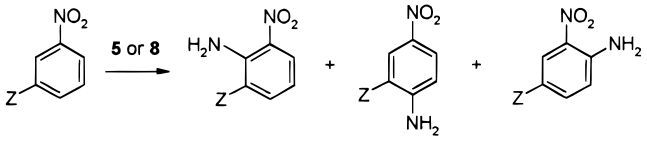
In contrast to the *ortho*-substituted nitrobenzenes, the *para*-substituted nitrobenzenes **17a**−**g** underwent amination with sulfenamide **8** in low yields (Table 2, entries 7, 10, and 11), whereas amination at position 2 with **5** proceeded satisfactorily (entries 4, 8, and 13). When substituent Z in the aromatic ring of **17** could function as a leaving group, the S_NAr reaction became the major competing process, but the yields of the VNS products **18d**, **18e**, and **18f** were acceptable (entries 5, 9, and 12). Two types of products of the S_NAr reaction were isolated: the "normal" products, containing the sulfenamide moiety (**19**, **23**), and 4-nitroaniline (**11**) which resulted from cleavage of the S−N bond (Table 2, entries 5, 6, and 11). A similar phenomenon was observed in the reaction of *o*-fluoronitrobenzene with **5** (Table 1, entry 7). The mechanism of formation of these products will be discussed later.

In the amination of *meta*-substituted nitrobenzenes **24a**−**k** with sulfenamides **5** and **8**, the orientation was a more complex problem because three isomeric products resulting from the substitution of hydrogen at positions 2, 4, and 6 could be formed (Table 3). Distribution of



the *ortho*- and *para*-aminated products, i.e., (**25** + **27**)/**26**, was a function of the structure of the sulfenamide and the reaction conditions. Amination of 3-nitrobenzonitrile (**24b**) with sulfenamide **5** took place preferentially at the *ortho* positions (Table 3, entry 3) whereas *para* orientation dominated with **8** (entries 4 and 5). There was no significant impact of the structure of the sulfenamide on the **25**/**27** ratio (*ortho* substitution). On the other hand, the ratio **25**/**27** was controlled by the type of substituent Z, as seen in the VNS reactions with carbanions.[7] Electron-withdrawing substituents, such as CN, COOMe, COPh, and CF_3, in the position 3 directedVNS substitution to position 6 to form **27** predominantly (entries 3, 6, 8, and 9), whereas Cl and MeO directed the substitution to position 2 to form **25** (entries 12 and 16). The influence of the reaction conditions was shown in the reaction of nitrobenzonitrile **24b** with **8**. When carried out in the presence of KOH, the 4-aminated product **26b** was selectively formed (entry 5). Likewise, EtONa increased the selectivity in amination of **24f** giving **26f** (entry 10). However, when KOH was used in

Table 3. Reactions of Sulfenamides 5 and 8 with 3-Substituted Nitrobenzenes

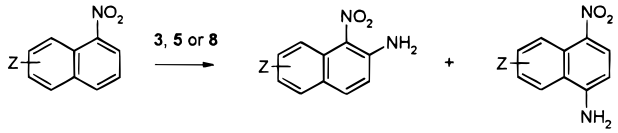


24a-k **25a-k** **26a-k** **27a-k**

entry	arene	Z	sulfenamide, conditions[a]	products of amination in position (yield, %) 2	4	6
1	**24a**	NO_2	**5**, A		**26a** (44)	
2			**8**, A		**26a** (11)	
3	**24b**	CN	**5**, A	**25b** (18)	**26b** (21)	**27b** (36)
4			**8**, A	**25b** (5)	**26b** (59)	**27b** (8)
5			**8**, B		**26b** (78)	
6	**24c**[b]	COOMe	**8**, A		**26c** (20[c])	**27c** (8)
7	**24d**	COOH	**8**, A		**26d** (18)	
8	**24e**	COPh	**8**, A		**26e** (28)	**27e** (21)
9	**24f**	CF_3	**8**, A		**26f** (29)	**27f** (6)
10			**8**, D		**26f** (84)	
11	**24g**	F	**8**, A		**26g** (66)	
12	**24h**	Cl	**5**, A	**25h** (26)	**26h** (38)	**27h** (7)
13			**8**, A		**26h** (86)	
14	**24i**	Br	**8**, A		**26i** (66)	
15	**24j**	Me	**8**, A		**26j** (56)	
16	**24k**	MeO	**5**, A	**25k** (46)	**26k** (21)	**27k** (4)
17			**8**, A		**26k** (48)	**27k** (12)
18			**8**, B			

[a] Procedures A, B, D: see Experimental Section. [b] The main product (**28**, 40%) resulted from reaction of **8** with the carbonyl group in **24c**. [c] Transesterification: methyl ester (**26c**, 15%) and *tert*-butyl ester (**26c′**, 5%).

Table 4. Reactions of Sulfenamides 3, 5, and 8 with 1-Nitronaphthalenes



2a-e **12a-e** **13a-e**

entry	arene	Z	sulfenamide, conditions[a]	products of amination in position (yield, %) 2	4	other products (yield, %)
1	**2**	H	**3**, A	**12** (71)	**13** (6)	
2			**3**, B	**12** (11)	**13** (75)	
3			**5**, A	**12** (63)	**13** (11)	
4			**5**, B	**12** (10)	**13** (26)	**29** (<1)
5			**8**, A	**12** (61)	**13** (24)	**29** (9)
6			**8**, B	**12** (2)	**13** (77)	
7			**8**, C	**12** (40)	**13** (16)	**30** (39)
8	**2a**	2-MeO	**8**, A		**13a** (88)	
9	**2b**	4-MeO	**8**, A	**12b** (68)		
10	**2c**	5-Br	**8**, A	**12c** (41)	**13c** (14)	**31** (28)
11	**2d**	5-($C_3H_5O_2$)[b]	**8**, A	**12d** (42)	**13d** (26)	**32** (8)
12	**2e**	5-aza[c]	**8**, A	**12e** (52)	**13e** (17)	**33** (29)
13			**8**, C	**12e** (24)	**13e** (8)	**33** (58)

[a] Procedures A, B, C: see Experimental Section. [b] **2d**: ethylene acetal of 1-nitro-5-naphthaldehyde. [c] **2e**: 5-nitroquinoline.

the case of less electrophilic *m*-nitroanisole, no reaction occurred (entry 18).

It should be noted that the amination of dinitroarenes with sulfenamides did not proceed satisfactorily. In the reactions of *o*- and *p*-dinitrobenzenes **1a** and **17a** with **5** and **8**, no expected dinitroanilines were produced. The dominating process was S_NAr substitution of the nitro group leading to the formation of **15** and **19** or the oxidation of the σ^H adduct leading to **14** (Tables 2 and 3, entries 1). These results are in accordance with the known difficulties in achieving VNS in *o*- and *p*-dinitrobenzenes.[17] *m*-Dinitrobenzene is known to be a very active partner in the VNS reaction,[18] but its amination with sulfenamides **5** and **8** proceeded in only moderate yield (Table 3, entries 1 and 2).

1-Nitronaphthalene (**2**) and its analogues **2a**−**f** reacted with sulfenamides even more readily than monocyclic nitroarenes, but the amination was often accompanied by the formation of nitrosonaphthylamines and naphthofurazans (Table 4). The main products in the reactions of substituted 1-nitronaphthalenes with sulfenamides **3**, **5**, and **8** were 2-amino and 4-amino derivatives **12** and **13**. The influence of the structure of the sulfenamide on the ratio of the isomeric products was much

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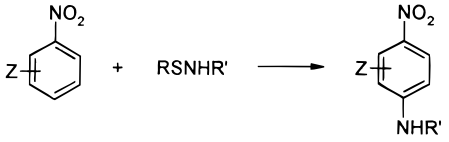
Table 5. Reactions of *N*-Substituted Sulfenamides with Nitroarenes



45a-j

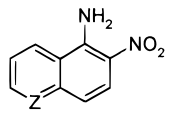
entry	arene	Z	sulfenamide, conditions[a]	R	R′	products (yield %)
1	**1c**	2-CF_3	**44**, A	Ph	Ph	**45a** (33)
2	**1e**	2-Cl	**42**, A	C_4H_8NCS[b]	cyclohexyl	**45b** (46)
3	**24b**	3-CN	**44**, A[c]	Ph	Ph	**45c** (45)
4	**24h**	3-Cl	**44**, A[c]	Ph	Ph	**45d** (52)
5			**44a**, C[c]	Ph	4-MeO−C_6H_4	**45e** (69)
6	**24i**	3-Br	**42**, A	C_4H_8NCS[b]	cyclohexyl	**45f** (66)
7	**24k**	3-MeO	**44a**, C[c]	Ph	4-MeO−C_6H_4	**45g** (33)
8	**2**	C_4H_4[d]	**42**, A	C_4H_8NCS[b]	cyclohexyl	(96) *e*
9			**43**, A	C_4H_8NCS[b]	Ph	**45j** (19)
10			**44**, B	Ph	Ph	**45j** (61)

[a] Procedures A, B, C: see Experimental Section. [b] *N*,*N*-Tetramethylenethiocarbamoil. [c] Conditions modified, see Experimental Section. [d] 1-Nitronaphthalene. [e] Total yield of two isomers: *N*-cyclohexyl-1-nitro-2-naphthylamine (**45h**, 70%) and *N*-cyclohexyl-1-nitro-4-naphthylamine (**45i**, 26%).

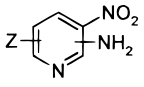
weaker here than in the case of nitrobenzenes but an increasing tendency for *para* substitution in the order **3**, **5**, and **8** was retained (Table 4, entries 1, 3, and 5). On the other hand, the effect of the reaction conditions on distribution of the 2- and 4-isomers was much stronger than that in the case of nitrobenzenes. The effect of the change of the base concentration was particularly evident in the reactions with 2-benzothiazolesulfenamide (**3**). This compound was not an effective aminating agent for mononitrobenzenes but reacted efficiently with nitronaphthalenes yielding mainly the 2-amino product **12** in the presence of *t*-BuOK/DMF whereas the 4-amino isomer **13** was formed predominantly when KOH/DMSO was used (Table 4, entries 1 and 2).

The amination of 2-nitronaphthalene (**34**) with **8** gave 2-nitro-1-naphthylamine (**35**) in 94% yield. This orientation was in agreement with all previous observations and mechanistic concepts indicating that position 1 in 2-nitronaphthalene is the most active toward nucleophilic attack.[7]

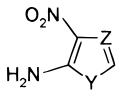
Amination of five- and six-membered heterocyclic compounds with sulfenamide **8** proceeded satisfactorily and similarly to VNS alkylation.[19,20] Orientation of the substitution corresponded to that reported for VNS with carbanions. *β*-Nitropyridines were aminated at positions activated by the nitro group: 4-ethoxy-3-nitropyridine (**36a**) and 2-methoxy-5-nitropyridine (**36b**) yielded the expected amino derivatives **37a** (75%) and **37b** (42%).



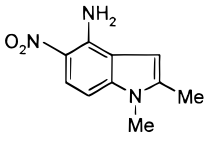
35: Z = CH
35a: Z = N



37a: 6-NH_2, Z = 4-EtO
37b: 2-NH_2, Z = 6-MeO



39a: Y = S, Z = CH
39b: Y = NMe, Z = N



41

The orientation pattern in these pyridine derivatives was explained in case of the carbanionic VNS reaction in terms of conjugation between the alkoxy and nitro groups.[21] Amination of 3-nitrothiophene (**38a**) gave the 2-amino derivative **39a** (23%) and similarly, the reaction with 1-methyl-4-nitroimidazole (**38b**) led to **39b** (36%). In cases where the heterocyclic ring was fused with a nitrobenzene ring, the reaction with **8** took place in the ring substituted with the nitro group. Amination of 5-nitroquinoline (**2e**) gave a mixture of nitro- and nitrosoaminoquinolines (Table 4, entries 12 and 13). 6-Nitroquinoline (**34a**) yielded the 5-amino derivative **35a** (98%), behaving analogously to 2-nitronaphthalene. 1,2-Dimethyl-5-nitroindole (**40**) underwent amination in the benzene ring giving **41** in moderate yield (45%), as could be expected for a less electrophilic nitroarene.

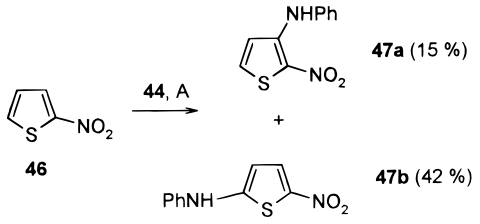
These results indicate that the reaction of carbo- and heterocyclic nitroarenes with sulfenamides **5** and **8** is an efficient method of synthesis of nitroarylamines via direct introduction of the amino group.

Alkyl- and Arylamination. *N*-Alkyl-substituted sulfenamides are readily available via oxidation of mixtures of thiols and primary amines, whereas *N*-aryl derivatives can be simply prepared via reaction of phenylsulfenyl chlorides with anilines.

N′-Cyclohexyl-*N*,*N*-tetramethylenethiocarbamoylsulfenamide (**42**), an *N*-alkyl derivative of the most efficient aminating agent **8**, reacted with substituted nitrobenzenes along the VNS amination pathway, yielding the corresponding *N*-cyclohexyl-4-nitroanilines (Table 5, entries 2 and 6). Also, the reaction of **42** with 1-nitronaphthalene gave the expected products of *N*-alkylamination (Table 5, entry 8). Despite the bulkiness of the *N*-cyclohexyl group which should increase steric hindrance, the ratio of the products of the reaction of **2** with **42** was almost identical to that observed in the reaction with **5** or **8** (cf., Table 4, entries 3 and 5). The results in Table 5 show that the reaction with *N*-alkyl sulfenamides is an efficient method of synthesis of alkylarylamines.

(19) (a) Mąkosza, M. *Synthesis* **1991**, 103. (b) Mąkosza, M.; Kwast, E. *Tetrahedron* **1995**, *51*, 8339.
(20) (a) Mąkosza, M.; Chylińska, B.; Mudryk, B. *Liebigs Ann. Chem.* **1984**, 8. (b) Mąkosza, M.; Sienkiewicz, K.; Wojciechowski, K. *Synthesis* **1990**, 850.
(21) Mąkosza, M.; Owczarczyk, Z. *J. Org. Chem.* **1989**, *54*, 5094.

Scheme 2



Arylamination with *N*-aryl sulfenamides posed some problems (Table 5) because an aryl substituent at the nitrogen diminished the nucleophilicity of the sulfenamide anion dramatically. The reaction of 1-nitronaphthalene with *N*,*N*-tetramethylenethiocarbamoylsulfenanilide (**43**) yielded the desired naphthylphenylamine **45j** in rather low yield (Table 5, entry 9). This problem was solved by using less acidic benzenesulfenanilides PhSNHAr where Ar = Ph (**44**) and *p*-MeO-C_6H_4 (**44a**). These sulfenamides were prepared via the reaction of benzenesulfenyl chloride PhSCl with aniline and *p*-anisidine.[22] The reaction of **44** with several nitroarenes yielded the expected diarylamines (Table 5, entries 1, 3, and 4). Compound **44a** was more desirable for arylamination of less electrophilic arenes such as 3-nitroanisole (**24k**), because of expected higher nucleophilicity of anion of **44a**. Thus **24k** which had not been efficiently aminated with **44** reacted satisfactorily with **44a** (Table 5, entry 7).

The VNS arylamination of substituted nitrobenzenes always occurred at position 4 (Table 5, entries 1, 3, 4, 5, and 7). This orientation is apparently due to the moderate nucleophilicity of the sulfenanilides which should promote formation of the thermodynamically controlled products (see the discussion below). The exception from this orientation pattern was 2-nitrothiophene (**46**) which in the reaction with **44** gave two isomers **47a** and **47b** (Scheme 2). The tendency for formation of the 4-substituted products in the arylamination of nitroarenes was enhanced when the reaction was carried out in KOH/DMSO (Table 5, entry 10), a result similar to that seen in the reactions with **5** and **8**.

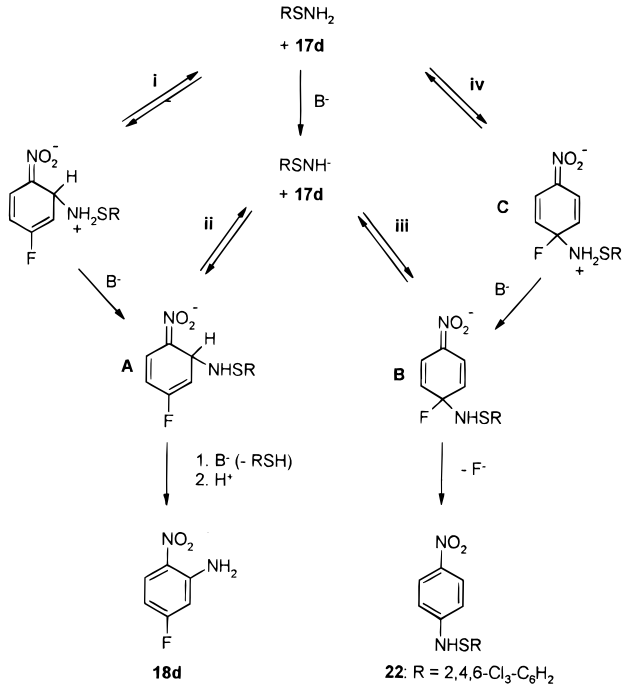
Mechanism. Although stoichiometry of the amination of nitroarenes with sulfenamides is analogous to the VNS alkylation and hydroxylation, its mechanistic features should be clarified independently. Existing data indicate that the VNS reactions with carbanions containing leaving groups X and with anions of alkyl hydroperoxides proceed via addition of these nucleophiles to nitroarenes with the formation of σ^H adducts followed by base induced β-elimination of HX or ROH. The elimination process gives nitrobenzylic carbanions or nitrophenolates which are protonated during the workup procedure.

Amination with sulfenamides is stoichiometrically similar to the amination with hydroxylamine. Although the latter process has been known for a long time, there is only one report on mechanistic studies of this reaction. Gitis and co-workers[23] proposed that the initial σ^H adducts were converted into the amination products via departure of OH anions with simultaneous intramolecular 1,2-hydride shift from the ring sp^3 carbon atom to the nitrogen, leading directly to the nitroaniline. They

(22) Lecher, H. *Chem. Ber.* **1925**, *58*, 409.

(23) Gitis, S. S.; Glaz, A. I.; Grigorev, V. V.; Kaminskii, A. Ya.; Martynenko, A. S.; Saukov, P. I. *Zh. Org. Khim.* **1967**, *3*, 1617; *Chem. Abstr.* **1968**, *68*, 12,104.

Scheme 3



confirmed this hypothesis by amination of perdeuterio *m*-dinitrobenzene with hydroxylamine in methanolic NaOH solution. Since the MS measurement indicated that the product contained five deuterium atoms (i.e., did not lose deuterium), the authors concluded that the reaction occurred via the 1,2-hydride shift.

In our opinion, those experiments cannot be considered as sufficiently diagnostic. The amino group in 2,4-dinitroaniline produced in the reaction is a strong *NH*-acid, and it should undergo fast proton exchange under the reaction conditions, so there is no reason to look for the deuterium in the amino group. We confirmed this in independent experiments in which 2,4-dinitroaniline underwent rapid *N*-deuteriation in NaOH/D_2O solution and *vice versa*: *N*-deuterated aniline lost deuterium when treated with NaOH/H_2O. Moreover, mass spectrometry is not a reliable tool to measure deuterium content in groups possessing labile protons, such as NH_2 in nitroanilines, because traces of water in the ionizing chamber could strongly affect the result. In conclusion, the experimental verification of the 1,2-hydride shift mechanism by Gitis is in our opinion invalid.

Possible mechanistic patterns for substitution of hydrogen and halogen in nitroarenes with sulfenamides are presented in Scheme 3. The first question is whether the σ^H adducts **A** are formed via path **i** or **ii**. Since the β-elimination of RSH from σ^H adducts requires strong base which can deprotonate the starting sulfenamide, a direct differentiation between paths **i** and **ii** cannot be made. The differentiation was made using S_NAr of fluorine in *p*-fluoronitrobenzene as the model process.

The substitution of fluorine proceeds via anionic σ^F adducts **B** which can be formed in two ways (paths **iii** and **iv**) that are analogous to paths **ii** and **i** in the σ^H adduct formation. Path **iii** can operate only when a base sufficiently strong for deprotonation of $RSNH_2$ to $RSNH^-$ is used, whereas formation of σ^F adduct **B** via path **iv** is possible in the presence of a much weaker base, e.g., triethylamine, which is able to deprotonate the much more acidic dipolar adduct **C**. It was found that the

reaction of *p*-fluoronitrobenzene with sulfenamide **8** did proceed in the presence of *t*-BuOK (Table 2, entry 7) and did not in the presence of Et_3N, so one can conclude that the substitution of fluorine occurred via path **iii**, namely, by addition of the sulfenamide anion followed by departure of F^- anion and that sulfenamide itself does not add to *p*-fluoronitrobenzene with formation of the dipolar σ^F adducts **C**. It is thus reasonable to assume that the formation of the anionic σ^H adducts proceeds via path **ii** rather than via path **i**.

The second question is how the σ^H adducts are converted into the VNS products. Since the reaction of α-halo carbanions and alkyl hydroperoxide anions proceed via base-induced *β*-elimination of HX from the σ^H adducts, the same pathway was expected here. The rate of such *β*-elimination depends on the base strength and concentration; thus the effect of the base on the rate of the process was studied using competition between S_NAr of halogen and VNS in *o*- and *p*-halonitrobenzenes.

In 4-fluoronitrobenzene (**17d**) there are two positions susceptible to a nucleophilic attack in the ring: position 4, which is occupied by fluorine, and position 2, occupied by hydrogen. Therefore two reactions with the sulfenamide anion could occur: VNS of the hydrogen leading to **18d** and S_NAr of the fluorine leading to **23** (Scheme 3). A competition between these reactions was indeed observed. The ratio of the products formed depended on the reaction conditions. When an excess of base in high concentration was present in the reaction mixture (*t*-BuOK in DMF), the arene **17d** reacted with the sulfenamide **5** yielding **18d** along with 4-nitroaniline (**11**), the S_NAr product (Table 2, entry 5). When a low concentration of the base was maintained (*t*-BuOK/DMF slowly added to a solution of the substrates), the yield of the VNS product **18d** was diminished and fluorine substitution leading to **23** dominated (entry 6). These results showed that a high base concentration increased the rate of the VNS reaction.

Analogously, the reaction of sulfenamide **5** with 4-chloronitrobenzene (**17e**), in which S_NAr of halogen proceeds slower than that in **17d**, gave selectively the VNS amination product **18e** under *t*-BuOK/DMF conditions (Table 2, entry 8). When the base was added continuously to the substrates, so its concentration was low throughout the reaction time, a mixture of **18e** and the S_NAr product **23** was formed (entry 9). The reaction with sulfenamide **8** in the *t*-BuOK/DMF system yielded the VNS product **18e** and the S_NAr product **19** (Table 2, entry 10). When the base was added slowly over the course of the reaction, a proportion of **19** increased (entry 11).

The results of competition between the substitution of hydrogen and the substitution of halogen were even more convincing for 2-halonitrobenzenes. We reported previously the results of the reaction of 2-fluoronitrobenzene (**1d**) with the sulfenamide **8**.[16] Under conditions A (*t*-BuOK/DMF) the formation of the VNS product **11d** dominated (Table 1, entry 8). When insoluble KOH was used as the base, the exclusive product was **15**, coming from S_NAr (entry 7). In the case of 2-chloronitrobenzene (**1e**) there was a similar effect, although shifted toward the VNS, due to the lower susceptibility of chlorine to nucleophilic substitution. The reaction of **1e** with the sulfenamide **8** and an excess of base yielded exclusively the VNS product **11e** (Table 1, entry 10). When a solution of *t*-BuOK in DMF was slowly added to a solution of the substrates, a mixture of **11e** and the S_NAr product **15** was formed (entry 9).

The changes of the VNS/S_NAr ratio in the reactions of halonitroarenes with sulfenamides indicated that in the case of hydrogen substitution (**ii**, Scheme 3), contrary to the halogen substitution (path **iii**), the rate of conversion of the σ^H adduct depended on the strength and concentration of the base. This conclusion strongly supports the hypothesis that the mechanism of the reaction includes base-promoted *β*-elimination, and this is consistent with the previous studies on the mechanisms of the VNS alkylation[24] and hydroxylation.[8]

Orientation. This mechanistic picture of the VNS amination of nitroarenes with sulfenamides coming from the studies of the competition between S_NAr of halogen and VNS of hydrogen was fully confirmed by the observed effect of the reaction conditions on the orientation of VNS. Numerous examples of the VNS amination presented in this paper indicate that its orientation is governed by three factors: the reaction conditions, structure of the sulfenamide, and substituents in the aromatic ring.

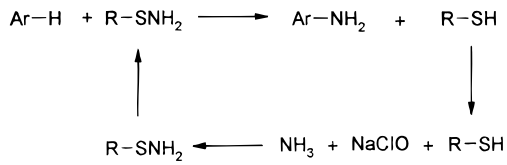
The influence of the reaction conditions was particularly notable in the case of the amination of 1-nitronaphthalene (**2**), which, independent of the structure of the sulfenamide, gave mostly the 2-amino derivative **12** in the presence of *t*-BuOK/DMF (Table 4, entries 1, 3, and 5) and the 4-amino derivative **13** when KOH/DMSO was used (Table 4, entries 2, 4, and 6). This effect of the type of the base on the orientation is analogous to that observed for the VNS hydroxylation of 1-nitronaphthalene with *tert*-butyl and cumyl hydroperoxides[8] and can be rationalized in a similar way. At a high concentration of the strong, soluble base (*t*-BuOK/DMF) the fast *β*-elimination of RSH from the σ^H adduct took place; thus the equilibration between the isomeric σ^H adducts at positions 2 and 4 was prevented. Since under these conditions the highly predominant product was the 2-amino isomer, one can conclude that the initial addition of the anion of **5** occurs at position 2. On the other hand, when the base was insoluble (KOH/DMSO) or it was present in a low concentration, elimination became slower and the system could equilibrate in favor of the more stable σ^H adduct leading to the 4-substituted product. Thus, 1-nitro-2-naphthylamine formed in the reaction with **3** or **5** in *t*-BuOK/DMF system was the product of kinetic control whereas 1-nitro-4-naphthylamine obtained in the reaction of **2** with **8** under KOH/DMSO conditions was the product of thermodynamic control. These reactions of amination of 1-nitronaphthalene can be considered as textbook examples of kinetic and thermodynamic control.

The orientation of the amination also depended on the type of aminating agent. Less acidic sulfenamides such as **3** and **5** led to preferential formation of the 2-amino isomer and sulfenamide **8**, which is probably more acidic so its anion is less nucleophilic than **3** and **5**, introduced the amino group into the *para* position.

Byproducts. The intriguing formation of 2- and 4-nitroanilines **10** and **11** in the reactions of compound **5** with 2- and 4-substituted nitrobenzenes **1d**, **17b**, **17d**, and **17f** (Table 1, entry 7, and Table 2, entries 2, 5, and 12) poses a question: in which way was the N−S bond broken so that simple nitroanilines were formed instead

(24) Mąkosza, M.; Glinka, T. *J. Org. Chem.* **1983**, *48*, 3860.

Scheme 4



of the expected S_NAr products *N*-(nitroaryl)sulfenamide **23** and its *ortho* isomer?

Compound **23**, synthesized by an alternate route, was stable under the reaction conditions and did not convert into **11**. Thus, the formation of nitroaniline **11** did not result from the decomposition of *N*-(nitroaryl)sulfenamide **23** and the S−N bond must thus have been cleaved in an earlier reaction step. The substitution of the cyano group in 4-nitrobenzonitrile **17b** is even more intriguing (Table 2, entry 2) because nucleophilic substitution of CN in a benzene ring is quite unusual.

Other interesting byproducts were 1-nitroso-2-naphthylamines (**30** and **31**) and naphthofurazans (**29** and **32**). The formation of naphthofurazans was observed earlier by Hasegawa[10,25] and by Nasielski-Hinkens[26] in their studies on amination of nitronaphthalenes and nitroquinolines with hydroxylamine and hydroxylamine-*O*-sulfonic acid. Formation of the same byproducts in those reactions justifies the supposition that the amination with sulfenamides and the amination with hydroxylamine proceed according to similar mechanisms.

Since few reactions of sulfenamide anions have been reported, one further example of nucleophilic reaction of $RSNH^-$ should be pointed out here: compound **8** reacts with methyl 3-nitrobenzoate **21c** to give mainly the *N*-acyl product **28** (Table 3, entry 6).

Conclusions

The vicarious nucleophilic substitution of hydrogen in nitroarenes with sulfenamides under basic conditions provides a new general way for synthesis of nitroanilines. Sulfenamide **8** is an efficient aminating agent in the synthesis of substituted *p*-nitroanilines, 1-nitro-4-naphthylamines, and aminoheterocycles. Introduction of the amino substituent at the position *ortho* to the nitro group is possible with sulfenamides **3** and **5**, **3** being preferred in the case of 1-nitronaphthalenes. Also, the new reaction offers opportunities of introduction of alkylamino and arylamino substituents into nitroarene rings.

The simplicity of the procedure and easy recycling of the aminating agent (Scheme 4) makes amination with sulfenamides an attractive method even for large scale preparations, because the only consumable reagents in the process are ammonia and sodium hypochlorite. If a method for the non-chlorine production of sulfenamides is found, the VNS amination can help avoid the use of chlorine in the manufacture of nitroanilines which are now obtained mainly via chloronitroarenes.[6]

Experimental Section[27]

Reagents. General procedure for synthesis of sulfenamides **3**-**9**.[15] The sodium salt of the thiol derivative, RSNa, (50 mmol), was dissolved in water (50 mL) and filtered. Then it was added to ammonia (25% solution in water, 13 mL) to which sodium hypochlorite (1 N solution in water, 55 mL) had been previously added slowly enough to maintain the temperature below 0 °C. The mixture was stirred vigorously for 30 min, and then the pure sulfenamide was filtered off. **3** was obtained from 2-mercaptobenzothiazole: mp 119−120 °C; lit.[15] mp 127−128 °C. **4** from 2,4-dichlorothiophenol: mp 56−60 °C. Anal. Calcd for $C_6H_5Cl_2NS$: C, 37.13; H, 2.60; N, 7.22. Found: C, 37.11; H, 2.63; N, 7.44. **5** from 2,4,6-trichlorothiophenol: mp 90−93 °C; lit.[28] mp 91−92 °C. **6** from 2-mercaptopyrimidine: mp 115−116 °C; lit.[29] mp 110−112 °C. **7** from thiobenzoic acid: mp 86−89 °C; lit.[30] mp 88.5−90 °C. **8** from ammonium *N*,*N*-tetramethylenedithiocarbamate: mp 84.5−85 °C.[31] Anal. Calcd for $C_5H_{10}N_2S_2$: C, 37.01; H, 6.21; N, 17.26. Found: C, 36.96; H, 6.09; N, 17.14. **9** from *O*-ethyl xanthate: oil.[32] Anal. Calcd for $C_3H_7NOS_2$: C, 26.26; H, 5.14; N, 10.21. Found: C, 25.91; H, 5.42; N, 9.79.

N′-Cyclohexyl-*N*,*N*-tetramethylenethiocarbamoylsulfenamide **42** was obtained by reaction of sodium *N*,*N*-tetramethylenedithiocarbamate with cyclohexylamine and iodine:[15] mp 59−61 °C; lit.[33] mp 65 °C. *N*,*N*-Tetramethylenethiocarbamoylsulfenanilide **43** was obtained by reaction of *N*,*N*-tetramethylenethiocarbamoyl disulfide with aniline catalyzed by silver nitrate:[34] mp 80−85 °C. Anal. Calcd for $C_{11}H_{14}N_2S_2$: C, 55.43; H, 5.92; N, 11.75. Found: C, 56.11; H, 6.25; N, 11.15. The sulfenanilides **44** and **44a** were obtained from benzenesulfenyl chloride and the respective aniline.[22] **44** from aniline: mp 52−55 °C; lit.[22] mp 53−55 °C. **44a** from *p*-anisidine: mp 60−64 °C; lit.[35] mp 69−70 °C. 2,4,6-Trichloro-4′-nitrobenzenesulfenanilide was obtained from 2,4,6-trichlorobenzenesulfenyl chloride and 4-nitroaniline[36] and proved to be identical with **23** by TLC and NMR.

Nitroarenes were commercially available or prepared according to the described procedures: 5-bromo-1-nitronaphthalene (**2c**),[37] 5-{2-(1,3-dioxolanyl)}-1-nitronaphthalene (**2d**),[38] 4-*tert*-butylnitrobenzene (**17g**),[39] 4-ethoxy-3-nitropyridine (**36a**),[40] 3-nitrothiophene (**38a**),[41] 1-methyl-4-nitroimidazole (**38b**),[42] 1,2-dimethyl-5-nitroindole (**40**).[43]

Reactions of Nitroarenes with Sulfenamides. The yields were not optimized. **A.** Nitroarene (2 mmol) and sulfenamide (2 mmol) dissolved in DMF (2 mL) were added dropwise, during 5 min, to a solution of *t*-BuOK (0.56 g, 5 mmol) in DMF (6 mL) at 20 °C. Stirring was continued for 15 min, and the mixture was poured into cold water (50 mL). Extraction with CH_2Cl_2, washing with water, drying with Na_2SO_4, and chromatography yielded products as yellow or orange crystals. **Modifications. 45c** (Table 5, entry 3): temp −25 °C. **45d** (Table 5, entry 4): temp −35 °C, stirring for 2 h. **47a**−**b** (Scheme 2): temp −25 °C, stirring for 5 min.

B. Nitroarene (2 mmol) and sulfenamide (2 mmol) dissolved in DMSO (2 mL) were added dropwise, during 5 min, to an intensively stirred suspension of powdered KOH (85%, 0.66

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(27) For general directions, see: Mąkosza, M.; Stalewski, J. *Tetrahedron* **1995**, *51*, 7263.
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(39) Shoesmith, J. B.; Mackie, A. J. *J. Chem. Soc.* **1928**, 2334.
(40) Bijlsma, U. G.; den Hertog, H. J. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 1187.
(41) Steinkopf, W.; Höpner, T. *Liebigs Ann. Chem.* **1933**, *501*, 174.
(42) Grimison, A.; Ridd, J. H.; Smith, B. V. *J. Chem. Soc.* **1960**, 1357.
(43) Noland, W. E.; Smith, L. R.; Johnson, D. C. *J. Org. Chem.* **1963**, *28*, 2262.

g, 10 mmol) in DMSO (6 mL) at 20 °C. Stirring was continued for 55 min and followed by workup as in **A**.

C. Nitroarene (2 mmol) and sulfenamide (2 mmol) dissolved in DMF (2 mL) were added dropwise, during 5 min, to a solution of *t*-BuOK (0.56 g, 5 mmol) in liquid ammonia (ca. 6 mL). Stirring was continued for 55 min, and then the ammonia was evaporated. Water (50 mL) was added followed by workup as in **A**. Modifications: **41e** and **41g** (Table 5, entries 5 and 7): stirring for 3 h.

D. Nitroarene (2 mmol) and sulfenamide (2 mmol) dissolved in DMF (2 mL) were added dropwise, during 5 min, to an intensively stirred suspension of EtONa (0.41 g, 6 mmol), in liquid ammonia (ca. 6 mL). Stirring was continued for 35 min followed by workup as in **C**.

Nitroarylamines. The ^{1}H NMR data were taken at 200 MHz in acetone-d_6 if not indicated otherwise. Coupling constants J are given in hertz. The signals of NH and NH_2 are not included as their chemical shifts vary over a wide range.

2-Nitroaniline (10): mp 69−71 °C; lit.[44] mp 70 °C; ^{1}H NMR δ 6.68 (m, 1H), 7.07 (dd, J = 8.6, 1.3, 1H), 7.41 (m, 1H), 8.04 (dd, J = 8.7, 1.5, 1H).

2-Nitro-3-trifluoromethylaniline (10c): mp 59−62 °C; lit.[44] mp 63−65 °C; ^{1}H NMR δ 7.10 (dm, J = 7.5, 1H), 7.34 (dm, J = 8.5, 1H), 7.50 (m, 1H).

4-Nitroaniline (11): mp 147−149 °C; lit.[44] mp 148 °C; ^{1}H NMR δ 6.75 (m, AA′ portion of AA′XX′ system, 2H), 8.00 (m, XX′ portion of AA′XX′ system, 2H).

3-Amino-6-nitrobenzonitrile (11b): mp 189−191 °C; lit.[44] mp 190−191 °C; ^{1}H NMR δ 7.03 (dd, J = 9.2, 2.6, 1H), 7.16 (d, J = 2.6, 1H), 8.16 (d, J = 9.2, 1H).

4-Nitro-3-trifluoromethylaniline (11c): mp 125−127 °C; lit.[44] mp 129−130 °C; ^{1}H NMR δ 6.94 (dd, J = 9.0, 2.6, 1H), 7.14 (d, J = 2.6, 1H), 7.97 (d, J = 9.0, 1H).

3-Fluoro-4-nitroaniline (11d): mp 159−161 °C; lit.[44] mp 161 °C; ^{1}H NMR (500 MHz) δ 6.52 (dd, J = 14.3, 2.4, 1H), 6.57 (ddd, J = 9.1, 2.4, 0.6, 1H), 7.92 (m, 1H).

3-Chloro-4-nitroaniline (11e): mp 156−159 °C; lit.[44] mp 158 °C; ^{1}H NMR δ 6.72 (dd, J = 9.0, 2.4, 1H), 6.84 (d, J = 2.4, 1H), 7.95 (d, J = 9.0, 1H).

3-Bromo-4-nitroaniline (11f): mp 170−172 °C, lit.[44] mp 176−178 °C; ^{1}H NMR δ 6.74 (dd, J = 9.0, 2.4, 1H), 7.05 (d, J = 2.4, 1H), 7.93 (d, J = 9.0, 1H).

3-Methoxy-4-nitroaniline {11g): mp 158−160 °C; lit.[44] mp 161 °C; ^{1}H NMR δ 3.86 (s, 3H), 6.31 (dd, J = 9.0, 2.2, 1H), 6.43 (d, J = 2.2, 1H), 7.84 (d, J = 9.0, 1H).

1-Nitro-2-naphthylamine (12): mp 123−125 °C; lit.[44] mp 123−124 °C; ^{1}H NMR δ 7.23 (d, J = 9.1, 1H), 7.35 (m, 1H), 7.60 (m, 1H), 7.79 (dd, J = 7.9, 1.5, 1H), 7.87 (d, J = 9.1, 1H), 8.58 (dm, J = 8.7, 1H).

4-Methoxy-1-nitro-2-naphthylamine (12b): mp 176−177 °C; ^{1}H NMR δ 4.05 (s, 3H), 6.64 (s, 1H), 7.35 (m, 1H), 7.62 (m, 1H), 8.11 (dd, J = 8.2, 1.5, 1H), 8.81 (d, J = 8.8, 1H). Anal. Calcd for $C_{11}H_{10}N_2O_3$: C, 60.55; H, 4.62; N, 12.84. Found: C, 60.40; H, 4.76; N, 12.75.

5-Bromo-1-nitro-2-naphthylamine (12c): ^{1}H NMR (DMSO-d_6, mixture with **13c**) δ 7.31 (d, J = 9.5, 1H), 7.46 (dd, J = 8.7, 7.6, 1H), 7.66 (dd, J = 7.6, 1.2, 1H), 8.12 (dd, J = 9.5, 0.7, 1H), 8.32 (dm, J = 8.7, 1H). Isolated as *N*-acetyl derivative: mp 191−194 °C; ^{1}H NMR δ 2.22 (s, 3H), 7.62 (dd, J = 8.7, 7.5, 1H), 7.83 (dm, J = 8.7, 1H), 7.98 (dd, J = 7.5, 1.0, 1H), 8.22 (d, J = 9.4, 1H), 8.45 (d, J = 9.4, 1H). Anal. Calcd for $C_{12}H_9BrN_2O_3$: C, 46.63; H, 2.93; N, 9.06. Found: C, 46.84; H, 3.11; N, 9.32.

6-Amino-5-nitro-1-naphthaldehyde ethylene acetal (12d): mp 159−161 °C; ^{1}H NMR δ 4.13 (m, 4H), 6.30 (s, 1H), 7.26 (d, J = 9.5, 1H), 7.59 (m, AB portion of ABX system, J = 7.4, 6.9, 1.1, 2H), 8.25 (d, J = 9.5, 1H), 8.46 (m, X portion of ABX system, J = 6.9, 1.1, 1H). Anal. Calcd for $C_{13}H_{12}N_2O_4$: C, 60.00; H, 4.65; N, 10.76. Found: C, 59.92; H, 4.71; N, 10.56.

5-Nitro-6-aminoquinoline (12e): mp 173−175 °C; lit.[44] mp 178 °C; ^{1}H NMR δ 7.50 (d, J = 9.4, 1H), 7.58 (dd, J = 8.8, 4.3, 1H), 7.98 (d, J = 9.4, 1H), 8.67 (dd, J = 4.3, 1.5, 1H), 9.01 (dm, J = 8.8, 1H).

1-Nitro-4-naphthylamine (13): mp 190−192 °C; lit.[44] mp 195 °C; ^{1}H NMR δ 6.83 (d, J = 8.8, 1H), 7.57 (m, 1H), 7.76 (m, 1H), 8.29 (d, J = 8.5, 1H), 8.40 (d, J = 8.8, 1H), 8.88 (dm, J = 8.8, 1H).

3-Methoxy-1-nitro-4-naphthylamine (13a): mp 162−163 °C; ^{1}H NMR δ 3.95 (s, 3H), 6.73 (s, 1H), 7.37 (m, 1H), 7.59 (m, 1H), 7.74 (m, 1H), 8.13 (m, 1H). Anal. Calcd for $C_{11}H_{10}N_2O_3$: C, 60.55; H, 4.62; N, 12.84. Found: C, 60.56; H, 4.59; N, 12.91.

8-Bromo-1-nitro-4-naphthylamine (13c): ^{1}H NMR (DMSO-d_6, mixture with **12c**) δ 6.84 (d, J = 9.1, 1H), 7.53 (dd, J = 8.9, 7.5, 1H), 7.83 (dd, J = 7.5, 1.2, 1H), 8.31 (d, J = 9.1, 1H), 8.81 (dd, J = 8.9, 1.2, 1H). Isolated as *N*-acetyl derivative: mp 188−190 °C; ^{1}H NMR δ 2.27 (s, 3H), 7.63 (dd, J = 8.7, 7.5, 1H), 8.05 (m, 1H), 8.07 (dd, J = 7.5, 1.1, 1H), 8.27 (d, J = 8.4, 1H), 8.38 (dd, J = 8.7, 1.1, 1H). Anal. Calcd for $C_{12}H_9BrN_2O_3$: C, 46.63; H, 2.93; N, 9.06. Found: C, 47.22; H, 3.21; N, 9.00.

8-Amino-5-nitronaphthaldehyde ethylene acetal (13d): mp 144−146 °C; ^{1}H NMR δ 4.26 (m, 4H), 6.63 (s, 1H), 6.88 (d, J = 8.8, 1H), 7.69 (dd, J = 8.8, 7.4, 1H), 7.97 (dd, J = 7.4, 1.0, 1H), 8.24 (d, J = 8.8, 1H), 8.82 (dd, J = 8.8, 1.0, 1H). Anal. Calcd for $C_{13}H_{12}N_2O_4$: C, 60.00; H, 4.65; N, 10.76. Found: C, 59.77; H, 4.57; N, 10.51.

5-Nitro-8-aminoquinoline (13e): mp 195−197 °C; lit.[44] mp 197 °C; ^{1}H NMR δ 6.97 (d, J = 9.0, 1H), 7.78 (dd, J = 8.9, 4.1, 1H), 8.50 (d, J = 9.0, 1H), 8.85 (dd, J = 4.1, 1.6, 1H), 9.35 (dd, J = 8.9, 1.6, 1H).

3,4-Dinitro-*N*-(*N*,*N*-tetramethylenethiocarbamoylthio)-aniline (14): mp 173 °C (dec); ^{1}H NMR δ 1.92−2.25 (m, 4H) 3.73 (t, J = 6.9, 2H), 3.81 (t, J = 7.0, 2H), 7.39 (dd, J = 9.0, 2.5, 1H), 7.46 (d, J = 2.5, 1H), 8.10 (d, J = 9.0, 1H). Anal. Calcd for $C_{11}H_{12}N_4O_4S_2$: C, 40.24; H, 3.68; N, 17.06. Found: C, 40.25; H, 3.58; N, 16.95.

2-Nitro-*N*-(*N*,*N*-tetramethylenethiocarbamoylthio)aniline (15): mp 138−140 °C; ^{1}H NMR (DMSO-d_6) δ 1.89 (m, 2H), 2.07 (m, 2H), 3.70 (m, 4H), 7.01 (m, 1H), 7.43 (dd, J = 8.6, 1.3, 1H), 7.61 (m, 1H), 8.06 (dd, J = 8.4, 1.5, 1H). Anal. Calcd for $C_{11}H_{13}N_3O_2S_2$: C, 46.63; H, 4.62; N, 14.83. Found: C, 46.53; H, 4.48; N, 14.71.

3-Amino-4-nitrobenzonitrile (18b): mp 128−131 °C;[45] ^{1}H NMR δ 6.99 (dd, J = 8.8, 1.7, 1H), 7.51 (d, J = 1.7, 1H), 8.21 (d, J = 8.8, 1H). Anal. Calcd for $C_7H_5N_3O_2$: C, 51.54; H, 3.09; N, 25.76. Found: C, 51.13; H, 3.16; N, 25.91.

2-Nitro-5-trifluoromethylaniline (18c): mp 98−101 °C; lit.[44] mp 103 °C; ^{1}H NMR δ 6.95 (dd, J = 8.9, 2.0, 1H), 7.47 (bs, 1H), 8.25 (d, J = 8.9, 1H).

3-Fluoro-6-nitroaniline (18d): mp 93−95 °C; lit.[44] mp 97 °C; ^{1}H NMR δ 6.49 (m, 1H), 6.80 (dd, J = 11.1, 2.7, 1H), 8.15 (dd, J = 9.5, 6.1, 1H).

3-Chloro-6-nitroaniline (18e): mp 128−129 °C; lit.[44] mp 128−129 °C; ^{1}H NMR δ 6.70 (dd, J = 9.2, 2.2, 1H), 7.15 (d, 2.2, 1H), 8.07 (d, J = 9.2, 1H).

3-Methoxy-6-nitroaniline (18f): mp 130−132 °C; lit.[44] mp 129−130.5 °C; ^{1}H NMR δ 3.84 (s, 3H), 6.29 (dd, J = 9.5, 2.7, 1H), 6.51 (d, J = 2.7, 1H), 8.00 (d, J = 9.5, 1H).

3-*tert*-Butyl-6-nitroaniline (18g): mp 90−91 °C; lit.[44] mp 91−92 °C; ^{1}H NMR δ 1.29 (s, 9H), 6.78 (dd, J = 9.1, 2.1, 1H), 7.07 (d, J = 2.1, 1H), 7.96 (d, J = 9.1, 1H).

(44) *Beilsteins Handbuch der Organischen Chemie:* compound **10** *Vol. 12*, E III, 1513; **10c** *Vol. 12*, E III, 2010; **11** *Vol. 12*, E III, 1580; **11b** *Vol. 14*, E III, 1021; **11c** *Vol. 12*, E III, 2011; **11d** *Vol. 12*, E III, 1648; **11e** *Vol. 12*, E III, 1665; **11f** *Vol. 12*, E III, 1676; **11g** *Vol. 13*, E I, 136; **12** *Vol. 12*, E II, 731; **12f** *Vol. 22*, E I, 639; **13** *Vol. 12*, E III, 2971; **13f** *Vol. 22*, E II, 357; **18c** *Vol. 12*, E III, 2010; **18d** *Vol. 12*, E III, 1646; **18e** *Vol. 12*, E III, 1655; **18f** *Vol. 13*, E III, 975; **18g** *Vol. 12*, H, 1166; **25h** *Vol. 12*, E III, 1658; **25k** *Vol. 13*, E II, 191; **26a** *Vol. 12*, E III, 1681; **26b** *Vol. 14*, E III, 980; **26c** *Vol. 14*, E I, 556; **26d** *Vol. 14*, E III, 980; **26f** *Vol. 12*, E III, 1944; **26g** *Vol. 12*, E III, 1647; **26h** *Vol. 12*, E III, 1662; **26i** *Vol. 12*, E III, 1675; **26j** *Vol. 12*, H, 846; **26k** *Vol. 13*, E III, 888; **27b** *Vol. 14*, E III, 1161; **27c** *Vol. 14*, E I, 583; **27e** *Vol. 14*, E I, 390; **27f** *Vol. 12*, E III, 2183; **27h** *Vol. 12*, E III, 1649; **27k** *Vol. 13*, E II, 286; **30** *Vol. 7*, H, 717; **35** *Vol. 12*, H, 1258; **35a** *Vol. 22*, E IV, 4680; **37b** *Vol. 22/11*, E V, 422; **45c** *Vol. 14*, E III, 984.

(45) Müller, E.; Hauel, N.; Noll, K.; Narr, B.; Heider, J.; Psiorz, M.; Bomhard, A.; Meel, V. J.; Diederen, W. GP 3,522,230, 1987; *Chem. Abstr.* **1987**, *106*, 156,466.

4-Nitro-*N*-(*N,N*-tetramethylenethiocarbamoylthio)aniline (19): mp 181−183 °C; ^{1}H NMR δ 1.91−2.24 (m, 4H), 3.72 (t, J = 6.8, 2H), 3.81 (t, J = 7.0, 2H), 7.18 (m, AA′ portion of AA′XX′, 2H), 8.12 (m, XX′ portion of AA′XX′ system, 2H). Anal. Calcd for $C_{11}H_{13}N_3O_2S_2$: C, 46.63; H, 4.62; N, 14.83. Found: C, 46.68; H, 4.55; N, 14.73.

2,4,6-Trichloro-4′-cyanobenzenesulfenanilide (21): mp 195−198 °C; ^{1}H NMR δ 7.33 (m, AA′ portion of AA′XX′ system, 2H), 7.59 (m, XX′ portion of AA′XX′ system, 2H), 7.60 (s, 2H). Anal. Calcd for $C_{13}H_7Cl_3N_2S$: C, 47.37; H, 2.14; N, 8.50. Found: C, 47.17; H, 1.95; N, 8.22.

2,4,6-Trichlorophenyl thiocyanate (22) was obtained from 2,4,6-trichloroaniline[46] and proved to be identical with a sample isolated from the reaction (Table 2, entry 2): mp 71−75 °C; ^{1}H NMR δ 7.84 (s, 2H). Anal. Calcd for $C_7H_2Cl_3NS$: C, 35.25; H, 0.85; N, 5.87. Found: C, 35.17; H, 0.79; N, 5.81.

2,4,6-Trichloro-4′-nitrobenzenesulfenanilide (23): mp 150 °C; ^{1}H NMR δ 7.35 (m, AA′ portion of AA′XX′ system, 2H), 7.60 (s, 2H), 8.12 (m, XX′ portion of AA′XX′ system, 2H). Anal. Calcd for $C_{12}H_7Cl_3N_2O_2S$: C, 41.23; H, 2.02; N, 8.01. Found: C, 42.18; H, 1.72; N, 7.98.

2-Amino-3-nitrobenzonitrile (25b): mp 129−130 °C;[47] ^{1}H NMR δ 6.90 (dd, J = 8.6, 7.5, 1H), 7.94 (dd, J = 7.5, 1.6, 1H), 8.40 (dd, J = 8.6, 1.6, 1H). Anal. Calcd for $C_7H_5N_3O_2$: C, 51.54; H, 3.09; N, 25.76. Found: C, 51.24; H, 2.80; N, 25.71.

2-Chloro-6-nitroaniline (25h): mp 73 °C; lit.[44] mp 72−73 °C; ^{1}H NMR δ 6.76 (dd, J = 8.7, 7.7, 1H), 7.68 (dd, J = 7.7, 1.5, 1H), 8.10 (dd, J = 8.7, 1.5, 1H).

2-Methoxy-6-nitroaniline (25k): mp 74−75.5 °C; lit.[44] mp 76 °C; ^{1}H NMR δ 3.95 (s, 3H), 6.64 (dd, J = 8.9, 7.8, 1H), 7.08 (dd, J = 7.8, 1.2, 1H), 7.65 (dd, J = 8.9, 1.2, 1H).

2,4-Dinitroaniline (26a): mp 180 °C, lit.[44] mp 181−182 °C; ^{1}H NMR δ 7.25 (d, J = 9.4, 1H), 8.21 (dd, J = 9.4, 2.7, 1H), 8.94 (d, J = 2.7, 1H).

2-Amino-5-nitrobenzonitrile (26b): mp 202−204 °C; lit.[44] mp 210 °C; ^{1}H NMR δ 7.04 (d, J = 9.4, 1H), 8.19 (dd, J = 9.4, 2.7, 1H), 8.38 (d, J = 2.7, 1H).

Methyl 2-amino-5-nitrobenzoate (26c): mp 169−170 °C; lit.[44] mp 168 °C; ^{1}H NMR δ 3.93 (s, 3H), 6.96 (d, J = 9.3, 1H), 8.11 (dd, J = 9.3, 2.7, 1H), 8.71 (d, J = 2.7, 1H).

***t*-Butyl 2-amino-5-nitrobenzoate (26c′):** mp 157−158 °C; ^{1}H NMR δ 1.63 (s, 9H), 6.94 (d, J = 9.3, 1H), 8.09 (dd, J = 9.3, 2.8, 1H), 8.67 (d, J = 2.8, 1H). Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 55.23; H, 6.01; N, 11.63.

2-Amino-5-nitrobenzoic acid (26d): mp 274−276 °C; lit.[44] mp 276 °C; ^{1}H NMR δ 6.97 (d, J = 9.3, 1H), 8.12 (dd, J = 9.3, 2.7, 1H), 8.78 (d, J = 2.7, 1H).

2-Amino-5-nitrobenzophenone (26e): mp 143−146 °C; lit.[48] mp 152−154 °C; ^{1}H NMR δ 7.07 (d, J = 9.3, 1H), 7.54−7.75 (m, 5H), 8.16 (dd, J = 9.3, 2.7, 1H), 8.39 (d, J = 2.7, 1H).

4-Nitro-2-trifluoromethylaniline (26f): mp 90−92 °C; lit.[44] mp 88 °C; ^{1}H NMR δ 7.05 (d, J = 9.2, 1H), 8.17 (dd, J = 9.2, 2.6, 1H), 8.30 (d, J = 2.6, 1H).

2-Fluoro-4-nitroaniline (26g): mp 125−128 °C; lit.[44] mp 134 °C; ^{1}H NMR δ 6.96 (m, 1H), 7.85−7.94 (m, 2H).

2-Chloro-4-nitroaniline (26h): mp 99−101 °C; lit.[44] mp 106−107 °C; ^{1}H NMR δ 6.98 (d, J = 9.0, 1H), 7.99 (dd, J = 9.0, 2.6, 1H), 8.15 (d, J = 2.6, 1H).

2-Bromo-4-nitroaniline (26i): mp 104−105 °C; lit.[44] mp 106−107 °C; ^{1}H NMR δ 6.98 (d, J = 9.1, 1H), 8.02 (dd, J = 9.1, 2.5, 1H), 8.30 (d, J = 2.5, 1H).

2-Methyl-4-nitroaniline (26j): mp 131−132 °C; lit.[44] mp 130 °C; ^{1}H NMR δ 2.23 (s, 3H), 6.76 (m, X portion of ABX system, 1H), 7.87−7.92 (m, AB portion of ABX system, 2H).

2-Methoxy-4-nitroaniline (26k): mp 140−141 °C; lit.[44] mp 139 °C; ^{1}H NMR δ 3.97 (s, 3H), 6.77 (d, J = 8.8, 1H), 7.64 (d, J = 2.4, 1H), 7.76 (dd, J = 8.8, 2.4, 1H).

4-Amino-3-nitrobenzonitrile (27b): mp 161−162 °C; lit.[44] mp 160 °C; ^{1}H NMR δ 7.23 (d, J = 8.9, 1H), 7.68 (dd, J = 8.9, 2.0, 1H), 8.47 (d, J = 2.0, 1H).

Methyl 4-amino-3-nitrobenzoate (27c): mp 204−207 °C; lit.[44] mp 199.5−200.0 °C; ^{1}H NMR δ 3.86 (s, 3H), 7.14 (d, J = 8.9, 1H), 7.93 (dd, J = 8.9, 2.0, 1H), 8.71 (d, J = 2.0, 1H).

4-Amino-3-nitrobenzophenone (27e): mp 139−141 °C; lit.[44] mp 140.5 °C; ^{1}H NMR δ 7.22 (d, J = 8.9, 1H), 7.52−7.80 (m, 5H), 7.93 (dd, J = 8.9, 2.1, 1H), 8.52 (d, J = 2.1, 1H).

2-Nitro-4-trifluoroaniline (27f): mp 102−105 °C; lit.[44] mp 109−110 °C; ^{1}H NMR δ 7.28 (d, J = 8.7, 1H), 7.67 (dd, J = 8.7, 2.1, 1H), 8.35 (bs, 1H).

4-Chloro-2-nitroaniline (27h): mp 105−110 °C; lit.[44] mp 116−117 °C; ^{1}H NMR δ 7.14 (d, J = 9.0, 1H), 7.42 (dd, J = 9.0, 2.5, 1H), 8.03 (d, J = 2.5, 1H).

4-Methoxy-2-nitroaniline (27k): mp 120−122 °C; lit.[44] mp 123 °C; ^{1}H NMR δ 3.79 (s, 3H), 7.05 and 7.14 (m, AB portion of ABX system, J = 9.2, 3.0, 0.4, 2H), 7.48 (m, X portion of ABX system, J = 3.0, 0.4, 1H).

3-Nitro-*N*-(*N,N*-tetramethylenethiocarbamoylthio)benzamide (28): mp 132−134 °C; ^{1}H NMR δ 2.01 (quintet, J = 5.5, 2H), 2.20 (quintet, J = 6.5, 2H), 3.70 (t, J = 6.8, 2H), 3.84 (t, J = 6.9, 2H), 7.88 (m, 1H), 8.45−8.52 (m, 2H), 8.89 (m, 1H). Anal. Calcd for $C_{12}H_{13}N_3O_3S_2$: C, 46.29; H, 4.21; N, 13.49. Found: C, 46.05; H, 4.46; N, 13.25.

Naphtho[1,2]furazan (29): 77−78 °C; lit.[49] mp 78−79 °C; ^{1}H NMR δ 7.75 (d, J = 9.4, 1H), 7.79−7.90 (m, 2H), 7.93 (d, J = 9.4, 1H), 8.02−8.08 (m, 1H), 8.56 (m, 1H).

1-Nitroso-2-naphthylamine (30): mp 147−149 °C; lit.[44] mp 150−152 °C; ^{1}H NMR (DMSO-d_6) δ 7.05 (d, J = 9.3, 1H), 7.47 (m, 1H), 7.66 (m, 1H), 7.81 (d, J = 7.8, 1H), (d, J = 9.3, 1H), 9.05 (d, J = 8.3, 1H). NOE was observed between signals δ 7.81 and 7.91.

5-Bromo-1-nitroso-2-naphthylamine (31): mp 193 °C (dec); ^{1}H NMR (500 MHz, CD_3CN) δ 7.10 (d, J = 9.5, 1H), 7.55 (dd, J = 8.4, 7.7, 1H), 7.78 (d, J = 7.7, 1H), 8.21 (d, J = 9.5, 1H), 9.25 (d, J = 8.4, 1H); HRMS (EI, 70 eV) calcd for $C_{10}H_7{}^{79}BrN_2O$ 249.9742, found 249.9738.

6-Naphtho[1,2]furazancarboxaldehyde ethylene acetal (32): mp 145−146 °C; ^{1}H NMR δ 4.20 (m, 4H), 6.39 (s, 1H), 7.80 (d, J = 9.9, 1H), 7.84 (m, 1H), 8.06 (d, J = 7.7, 1H), 8.31 (d, J = 9.9, 1H), 8.61 (dm, J = 7.8, 1H). Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56. Found: C, 64.25; H, 3.85; N, 11.44.

5-Nitroso-6-aminoquinoline (33): mp 176 °C (dec); ^{1}H NMR δ 7.38 (d, J = 9.5, 1H), 7.69 (dd, J = 8.4, 4.4, 1H), 8.02 (dd, J = 9.5, 0.7, 1H), 8.81 (dd, J = 4.4, 1.7, 1H), 9.53 (d, J = 8.4, 1H); HRMS (EI, 70 eV) calcd for $C_9H_7N_3O$ 173.0589, found 173.0582.

2-Nitro-1-naphthylamine (35): mp 144−146 °C; lit.[44] mp 144 °C; ^{1}H NMR δ 7.14 (dm, J = 9.5, 1H), 7.62 (m, 1H), 7.72 (m, 1H), 7.88 (dd, J = 8.0, 1.6, 1H), 8.06 (d, J = 9.5, 1H), 8.50 (dm, J = 8.3, 1H).

6-Nitro-5-aminoquinoline (35a): mp 281−285 °C; lit.[44] mp 272−273 °C; ^{1}H NMR (acetone-d_6/DMSO-d_6) δ 7.18 (dd, J = 9.7, 0.7, 1H), 7.58 (dd, J = 8.6, 4.3, 1H), 8.25 (d, J = 9.7, 1H), 8.98 (dd, J = 4.3, 1.6, 1H), 9.06 (dm, J = 8.6, 1H).

2-Amino-4-ethoxy-5-nitropyridine (37a): mp 218−220 °C; ^{1}H NMR δ 1.42 (t, J = 7.0, 3H), 4.18 (q, J = 7.0, 2H), 6.23 (s, 1H), 8.64 (s, 1H). Anal. Calcd for $C_7H_9N_3O_3$: C, 45.90; H, 4.95; N, 22.94. Found: C, 46.02; H, 4.70; N, 22.79.

2-Amino-6-methoxy-3-nitropyridine (37b): mp 169−171 °C; lit.[44] mp 171−172 °C; ^{1}H NMR δ 3.91 (s, 3H), 6.16 (d, J = 9.1, 1H), 8.30 (d, J = 9.1, 1H).

2-Amino-3-nitrothiophene (39a): mp 168−171 °C; lit.[50] mp 150−153 °C; ^{1}H NMR δ 6.42 (d, J = 6.2, 1H), 7.13 (d, J = 6.2, 1H).

1-Methyl-4-nitro-5-aminoimidazole (39b): mp 299 °C (dec), lit.[51] mp 303 °C; ^{1}H NMR (DMSO-d_6) δ 3.43 (s, 3H), 7.25 (s, 1H).

1,2-Dimethyl-4-amino-5-nitroindole (41): mp 166−168 °C; ^{1}H NMR δ 2.41 (s, 3H), 3.71 (s, 3H), 6.68 (m, 1H), 6.75 (d, J = 9.4, 1H), 7.82 (d, J = 9.4, 1H). Anal. Calcd for

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$C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.68; H, 5.16; N, 19.79.

4-Nitro-*N*-phenyl-3-trifluoromethylaniline (45a): mp 154−155 °C; lit.[52] mp 149−150 °C; ^{1}H NMR δ 7.15−7.23 (m, 1H), 7.31−7.49 (m, 6H), 8.10 (d, J = 9.0, 1H).

3-Chloro-*N*-cyclohexyl-4-nitroaniline (45b): mp 92−93 °C; ^{1}H NMR δ 1.16−1.81 (m, 10H), 3.37−3.55 (m, 1H), 6.66 (dd, J = 9.2, 2.5, 1H), 6.74 (d, J = 2.5, 1H), 7.95 (d, J = 9.2, 1H). Anal. Calcd for $C_{12}H_{15}ClN_2O_2$: C, 56.59; H, 5.94; N, 11.00. Found: C, 56.87; H, 5.98; N, 10.76.

5-Nitro-2-(phenylamino)benzonitrile (45c): mp 165−167 °C; lit.[44] mp 171 °C; ^{1}H NMR δ 7.17−7.53 (m, 5H), 7.19 (d, J = 9.5, 1H), 8.25 (dd, J = 9.5, 2.7, 1H), 8.50 (d, J = 2.7, 1H).

2-Chloro-4-nitro-*N*-phenylaniline (45d): mp 111−112 °C; lit.[53] mp 112−113 °C; ^{1}H NMR δ 7.16−7.29 (m, 1H), 7.18 (d, J = 9.2, 1H), 7.34−7.50 (m, 4H), 8.04 (dd, J = 9.2, 2.6, 1H), 8.25 (d, J = 2.6, 1H).

2-Chloro-*N*-(4-methoxyphenyl)-4-nitroaniline (45e): mp 112−113 °C; lit.[53] mp 99−100 °C; ^{1}H NMR δ 3.84 (s, 3H), 6.92 (m, 1H), 7.03 (m, AA′ portion of AA′BB′, 2H), 7.29 (m, BB′ portion of AA′BB′, 2H), 8.01 (dd, J = 9.3, 2.6, 1H), 8.23 (d, J = 2.6, 1H).

2-Bromo-*N*-cyclohexyl-4-nitroaniline (45f): mp 90−91 °C; ^{1}H NMR δ 1.22−1.83 (m, 10H), 3.60 (m, 1H), 6.89 (d, J = 9.3, 1H), 8.08 (dd, J = 9.3, 2.6, 1H), 8.30 (d, J = 2.6, 1H). Anal. Calcd for $C_{12}H_{15}BrN_2O_2$: C, 48.18; H, 5.05; N, 9.36. Found: C, 48.08; H, 5.07; N, 9.63.

2-Methoxy-*N*-(4-methoxyphenyl)-4-nitroaniline (45g): dark orange oil; ^{1}H NMR δ 3.82 (s, 3H), 4.02 (s, 3H), 6.91 (m, 1H), 6.99 (m, AA′ portion of AA′BB′, 2H), 7.27 (m, BB′ portion of AA′BB′, 2H), 7.71 (d, J = 2.4, 1H), 7.79 (dd, J = 9.0, 2.4, 1H). Anal. Calcd for $C_{14}H_{14}N_2O_4$: C, 61.31; H, 5.14; N, 10.21. Found: C, 61.17; H, 5.02; N, 10.32.

***N*-Cyclohexyl-1-nitro-2-naphthylamine (45h):** mp 104−106 °C; ^{1}H NMR δ 1.30−1.87 (m, 10H), 3.86 (m, 1H), 7.35 (m, 1H), 7.38 (d, J = 9.4, 1H), 7.60 (m, 1H), 7.80 (dd, J = 7.9, 1.5, 1H), 7.96 (d, J = 9.4, 1H), 8.60 (dm, J = 8.8, 1 H); NOE was observed between signals δ 7.80 and 7.96 (500 MHz). Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.06; H, 6.83; N, 10.36.

***N*-Cyclohexyl-1-nitro-4-naphthylamine (45i):** mp 148−150 °C; ^{1}H NMR δ 1.22−1.88 (m, 10H), 3.74 (m, 1H), 6.75 (d, J = 9.0, 1H), 7.53 (m, 1H), 7.73 (m, 1H), 8.31 (dm, J = 8.6, 1H), 8.45 (d, J = 9.0, 1H), 8.97 (dd, J = 8.8, 1.3, 1H). Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.90; H, 6.89; N, 10.31.

1-Nitro-*N*-phenyl-4-naphthylamine (45j): mp 157−158 °C; ^{1}H NMR (500 MHz) δ 7.16 (d, J = 8.9, 1H), 7.17−7.23 (m, 1H), 7.41−7.48 (m, 4H), 7.66 (m, 1H), 7.81 (m, 1H), 8.36 (d, J = 8.9, 1H), 8.48 (d, J = 8.6, 1H), 8.87 (dm, J = 8.8, 1H). Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.51; H, 4.37; N, 10.64.

2-Nitro-3-(phenylamino)thiophene (47a): mp 103−105 °C; lit.[54] mp 104 °C; ^{1}H NMR δ 7.05 (d, J = 6.1, 1H), 7.23−7.31 (m, 1H), 7.41−7.49 (m, 4H), 7.81 (d, J = 6.1, 1H).

2-(Phenylamino)-5-nitrothiophene (47b): mp 186 °C; lit.[55] mp 193 °C; ^{1}H NMR δ 6.52 (d, J = 4.8, 1H), 7.15 (m, 1H), 7.34−7.50 (m, 4H), 7.85 (d, J = 4.8, 1H).

JO970582B

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