Oxidative Nucleophilic Substitution of Hydrogen in Nitroarenes

Mieczysław Mąkosza* and Krzysztof Staliński

Dedicated to Professor Dieter Seebach on the occasion of his 60th birthday

Abstract: Carbanions of 2-phenylpropio-nitrile were found to add to nitroarenes in liquid ammonia to form σ^H adducts, which were oxidized with $KMnO_4$ to yield products of oxidative nucleophilic substitution of hydrogen (ONSH) in the position *para* to the nitro group. Treatment of the carbanion–nitroarene system with methyl iodide at $-70\,°C$ indicated that the addition proceeds almost to comple-tion. Thus, for the first time, the persis-tence of σ^H adducts, formed between free

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anions and mononitroarenes, has been demonstrated. It was also shown that $KMnO_4$ oxidizes σ^H adducts to nitroben-zene faster than it does carbanions. This selective ONSH in the *para* positions of nitroarenes is a general process. However, some substituents hinder or inhibit the ox-idation step.

Introduction

The nucleophilic aromatic substitution of halogens or other nu-cleofugal groups in electrophilic arenes such as nitroarenes, pro-ceeding through the S_NAr addition–elimination mechanism, is of great practical value, and its mechanism has been thoroughly investigated.[1]

Only recently it was recognized that parallel to this classical reaction there is a possibility of nucleophilic substitution of hydrogen and that this process can be the major reaction path-way.[2, 3] Moreover it was shown that the classical S_NAr of halo-gen is, in fact, a secondary process, preceded by a reversible addition of nucleophiles to the ring carbon atoms bearing hy-drogen and formation of anionic σ^H adducts. These σ^H adducts can react further in a variety of ways, to give products of nucleo-philic substitution of hydrogen, or dissociate to the starting reagents when the former is not possible; formation of the iso-meric σ^X adducts can then take place and ultimately S_NAr sub-stitution of halogen.[3]

Amongst the many pathways available for the conversion of the σ^H adducts, the most obvious appears to be removal of the hydride anions by oxidation, which results in oxidative nucle-ophilic substitution of hydrogen (ONSH). Although many ex-amples of this transformation have been reported, it suffers from some limitations. The most important of these is the sensi-tivity of nucleophilic agents towards oxidation. This, in connec-tion with often unfavorable position of the addition equilibrium and hence low concentration of the σ^H adducts and high concen-tration of the nucleophiles, leads to undesired oxidation of nu-cleophiles and suppression of the ONSH reaction. Also, an im-portant requirement for successful reaction is that the rate of oxidation of the σ^H adducts should be high; otherwise, compet-ing processes such as S_NAr of a leaving group or single-electron transfer can dominate. We have formulated some guidelines concerning the nature of the nucleophiles, electrophilic arenes, and reaction conditions, designed to help predict the feasibility of the ONSH process for a given system.[3b, c] For example, ONSH can proceed satisfactorily when nucleophiles, such as OH^- or NH_3, are resistant towards oxidation, when the equi-librium of the nucleophilic addition is shifted towards the ad-ducts because of the high electrophilicity of the arene, or when specific features of the nucleophiles ensure that the σ^H adducts are present in high concentration.

Results and Discussion

Apart from adjusting the nature of the nucleophile and arene, as outlined in the Introduction, one might also expect that it should be possible to find an oxidant that would oxidize the σ^H adduct faster than the nucleophile, in spite of generally high sensitivity of the latter towards oxidation. In our search for such an oxidant, we reasoned that electrostatic repulsion between anionic nucleophiles and anionic oxidants should decelerate the undesired oxidation of the former, and that the repulsion should be much weaker in the case of the anionic σ^H adducts, in which the negative charge is highly delocalized. Thus, the latter should be oxidized more rapidly.

It has been known for many years that $KMnO_4$ in liquid ammonia is an excellent oxidant for σ^H adducts formed by addi-tion of ammonia and amide anion to electrophilic arenes, partic-ularly heteroarenes.[4] This oxidative variant of the Chichibabin reaction, introduced into organic synthesis by van der Plas, is a

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general process of great practical value.[2] Since $KMnO_4$ in liquid ammonia forms rather loose ion pairs, as do the sodium or potassium salts of carbanions, we expected that some highly nucleophilic carbanions could be indentified, which, although readily oxidized with oxygen, should be more resistant towards oxidation with $KMnO_4$ owing to electrostatic repulsion. In contrast, the corresponding σ^H adducts should be rapidly oxidized with this oxidant. Indeed, as we reported in a preliminary communication, treatment of a mixture of 2-phenylpropionitrile carbanion (1^-) and nitrobenzene ($2a$) in liquid ammonia with potassium permanganate leads to the ONSH product $3a$ in high yield (Scheme 1).[5]

Further studies have shown that this process is general for nitrobenzene derivatives and proceeds selectively *para* to the nitro group. Under optimized conditions ($T = -70\,°C$; molar ratio $1:2a:KMnO_4$, $1:1:0.75$) yields of the ONSH product are usually excellent. Results of the ONSH reaction of 1 with a selection of nitroarenes are given in Table 1. In a series of exper-

Abstract in Polish: *Karboanion 2-fenylopropionitrylu przyłącza się w ciekłym amoniaku do nitro-arenów tworząc addukty σ^H, które ulegają utlenieniu $KMnO_4$ tworząc produkty oksydatywnego nukleofilowego podstawienia wodoru w pozycji para do grupy nitrowej. Działaniem jodkiem metylu na układ: karboanion-nitroaren wykazano, że w $-70\,°C$ następuje praktycznie całkowite przyłączenie karboanionu do nitroarenu. Tak więc po raz pierwszy udowodniono, że addukty σ^H karboanionów do mononitroarenów mają długi czas życia. Wykazano również, że $KMnO_4$ w ciekłym amoniaku utlenia szybciej addukt σ^H do nitrobenzenu niż karboanion oraz, że niektóre podstawniki w pierścieniu aromatycznym inhibują proces utleniania adduktów σ^H.*
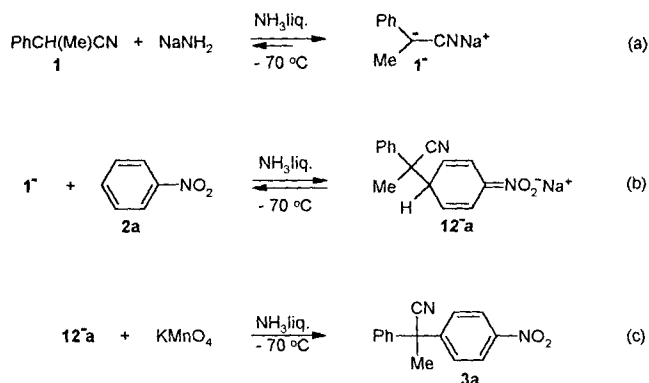
Scheme 1. Oxidative nucleophilic substitution of hydrogen in nitrobenzene with $KMnO_4$ as the oxidant.

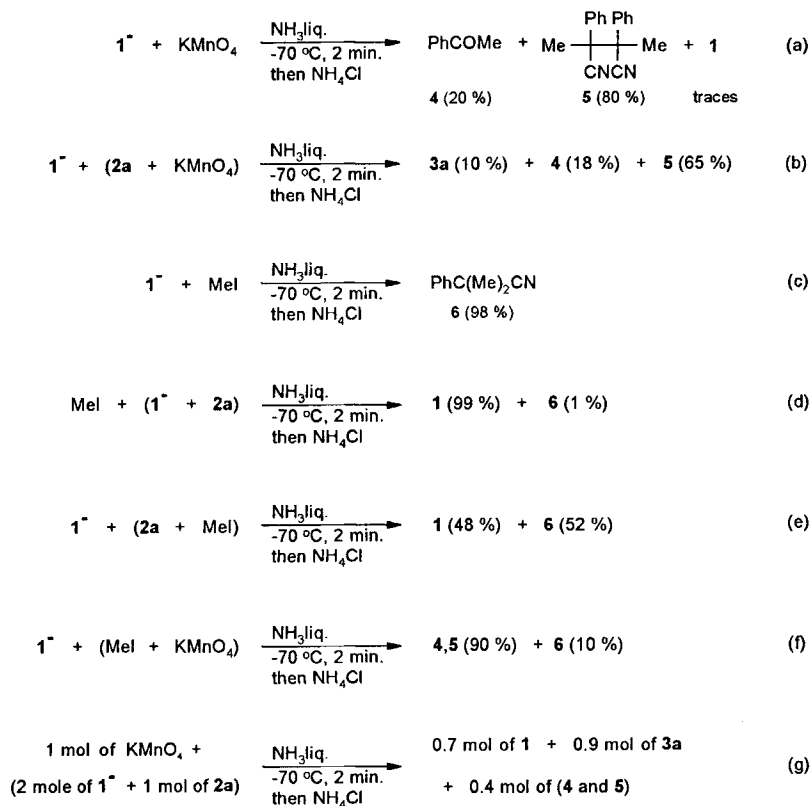Table 1. The ONSH reaction of 1^- with a selection of nitroarenes $2a-r$ (see Scheme 1).

X	Y	Yield 12^- [a]	Product	Yield [b]	r [c]
H	H	99	3a	90	0.91
2-F	H	99	3b	61	0.62
3-F	H	99	3c	96	0.97
2-Cl	H	99	3d	78	0.79
3-Cl	H	97	3e	90	0.93
2-Br	H	99	3f	84	0.85
3-Br	H	95	3g	78	0.82
2-I	H	98	3h	85	0.87
3-I	H	96	3i	47	0.49
3-F	5-F	99	3j	61	0.62
2-Cl	5-Cl	99	3k	46	0.47
3-Cl	5-Cl	99	3l	traces	0.01
2-Br	5-Br	99	3m	33	0.33
3-F	5-I	99	3n	9	0.09
2-MeO	H	82	3o	63	0.77
3-MeO	H	99	3p	68	0.69
3-CN	H	99	3r	67	0.68

[a] Percentage estimated by reaction with MeI according to Scheme 2, reaction c. [b] Yields (%) are of isolated products, except $3l$; when the yield of 3 was low (e.g. $3l$, $3n$), 1 and the nitroarene were recovered; in all cases, over 90% of the starting material was accounted for. [c] r = yield of 3/percentage 12^- formed.

iments it was shown that 0.75 equiv of oxidant is sufficient; nevertheless, the results reported in Table 1 were obtained for the ratio $1:1:1$. Although it has already been reported that such carbanions react with nitrobenzene to give ONSH products in moderate yields even in the absence of an external oxidant,[6] the rate of this spontaneous oxidation reaction is much slower. Under the conditions (i.e. temperature, solvent, and reaction time) used in this paper, the conversion without added $KMnO_4$ was negligible (below $1-2\%$).

We decided to carry out a series of experiments with nitrobenzene, in order to verify our hypothesis concerning the the relative rates of oxidation of the nucleophile and the σ^H adduct and to investigate further specific features of this reaction. The results are presented in Scheme 2. The notation $A + (B + C)$ indicates that reagent A was added to a mixture of $B + C$ two minutes after B and C had been mixed.

On the basis of reaction a in Scheme 2 (reaction $2a$), we can conclude that oxidation of carbanions 1^- with potassium per-

1⁻ + KMnO₄ $\xrightarrow[\text{then NH}_4\text{Cl}]{\substack{\text{NH}_3\text{liq.}\\-70\ ^\circ\text{C, 2 min.}}}$ PhCOMe + Me—(CPh Ph / CNCN)—Me + 1   (a)
   4 (20 %)   5 (80 %)   traces

1⁻ + (2a + KMnO₄) $\xrightarrow[\text{then NH}_4\text{Cl}]{\substack{\text{NH}_3\text{liq.}\\-70\ ^\circ\text{C, 2 min.}}}$ 3a (10 %) + 4 (18 %) + 5 (65 %)   (b)

1⁻ + MeI $\xrightarrow[\text{then NH}_4\text{Cl}]{\substack{\text{NH}_3\text{liq.}\\-70\ ^\circ\text{C, 2 min.}}}$ PhC(Me)₂CN   (c)
   6 (98 %)

MeI + (1⁻ + 2a) $\xrightarrow[\text{then NH}_4\text{Cl}]{\substack{\text{NH}_3\text{liq.}\\-70\ ^\circ\text{C, 2 min.}}}$ 1 (99 %) + 6 (1 %)   (d)

1⁻ + (2a + MeI) $\xrightarrow[\text{then NH}_4\text{Cl}]{\substack{\text{NH}_3\text{liq.}\\-70\ ^\circ\text{C, 2 min.}}}$ 1 (48 %) + 6 (52 %)   (e)

1⁻ + (MeI + KMnO₄) $\xrightarrow[\text{then NH}_4\text{Cl}]{\substack{\text{NH}_3\text{liq.}\\-70\ ^\circ\text{C, 2 min.}}}$ 4,5 (90 %) + 6 (10 %)   (f)

1 mol of KMnO₄ + (2 mole of 1⁻ + 1 mol of 2a) $\xrightarrow[\text{then NH}_4\text{Cl}]{\substack{\text{NH}_3\text{liq.}\\-70\ ^\circ\text{C, 2 min.}}}$ 0.7 mol of 1 + 0.9 mol of 3a + 0.4 mol of (4 and 5)   (g)

Scheme 2. Mechanistic investigations of the reaction shown in Scheme 1 (in reactions b, d, e, and g, the percentage of recovered 2a is omitted for clarity; see Experimental Section for details).

manganate in liquid ammonia is a fast process, producing acetophenone (4) and the dimerization product 5 in a ratio of approximately 1:4. Indeed, reaction 2b shows that it proceeds faster than the addition of 1⁻ to 2a: when 1⁻ was added to an equimolar mixture of nitrobenzene and KMnO₄, the major process was oxidation of the carbanion to give 4 and 5, and only small amounts of 3a and therefore the σ^H adduct were formed. The high rate of oxidation of the carbanion and very efficient oxidation of the σ^H adduct when 1⁻ and 2a were mixed in advance (Scheme 1) suggest that equilibrium 1b is shifted to the right and that the σ^H adduct 12⁻a is present in high concentration. Looking for an independent method of confirming the high σ^H adduct concentration, we chose to add MeI to the mixture, since this reagent reacts rapidly with the carbanion but not with the σ^H adduct. Reaction 2c was first used to show that the methylation of 1⁻ proceeds rapidly and quantitatively under the standard conditions. However, when MeI was added to an equimolar mixture of 1⁻ and 2a only 1% of the carbanion was alkylated, and the starting nitrile was recovered almost quantitatively upon quenching with NH₄Cl (reaction 2d). This indicates that most of the carbanion in the equilibrated reaction mixture was reversibly bound by nitrobenzene, obviously in the form of the σ^H adduct. Variation of the ratio 1⁻ and 2a in reaction 2d and also of the reaction time confirmed that nitrobenzene does not inhibit the alkylation; it simply reversibly adds close to an equimolar amount of the carbanion. Reaction 2e shows that the methylation of 1⁻ with MeI and its addition to nitrobenzene occur at similar rates. Reaction 2f indicates that oxidation of 1⁻ proceeds faster than its alkylation: when 1⁻ was added to an equimolar mixture of MeI and KMnO₄ the
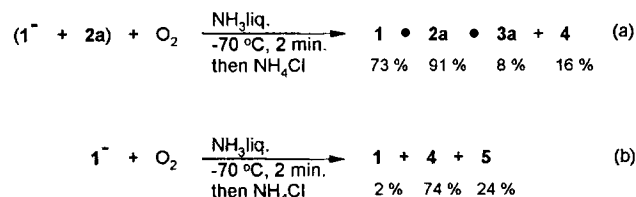
dominant process was oxidation of the carbanion to give 4 and 5, whereas alkylation of 1⁻ was much more slower. Thus, for the first time it has been unambiguously shown that σ^H adducts, formed from relatively free anionic species (i.e. loose ion pairs) and mononitroarenes, are present in high concentration in a highly polar solvent.

A further important question concerns the relative rates of oxidation of 1⁻ and σ^H adduct 12⁻a with KMnO₄. According to our initial hypothesis the oxidation of 1⁻ with anionic oxidant MnO₄ should be somewhat hindered by electrostatic repulsion, and the σ^H adduct, in which the negative charge is highly delocalized, should be oxidized faster. This hypothesis appears doubtful in the light of the high rate of the carbanion oxidation (reaction 2b). Nevertheless, results of the experiments presented in equation 2g confirm this hypothesis. Here, a mixture of 2 mol of 1⁻ and 1 mol of 2a was prepared. Given the practically complete conversion of 1⁻ and 2a into 12⁻a when present in equimolar amounts in the equilibrated system (reaction 2d), there should be practically equal concentrations of 1⁻ and σ^H adduct 12⁻a in the above mixture. Upon addition of less than 1 mol of KMnO₄, a substantial amount of 3a was formed. This result indicates that oxidation of σ^H adduct proceeds faster than that of 1⁻. Thus, our initial hypothesis that KMnO₄ should oxidize 12⁻a faster than 1⁻ is correct, although there is no doubt that the high concentration of 12⁻a in this system is the major factor responsible for the successful ONSH reaction.

There are numerous reports on the oxidation of carbanion–nitroarene σ^H adducts in which the oxidation agent was oxygen[2, 7] or was not unambiguously identified.[8] It appears that oxidation with oxygen proceeds particularly well for σ^H adducts of secondary carbanions in the presence of an excess of base. This suggests that the species actually being oxidized are the dianions produced by deprotonation of the σ^H adducts.[7a] We attempted to achieve ONSH in nitrobenzene with 1 using oxygen as the oxidant (Scheme 3). The oxidation of the σ^H adduct 12⁻a with oxygen was found to be slow (reaction 3a), and the oxidation of the carbanion 1⁻ fast (reaction 3b). It should be also noted that oxidation of 1⁻ with oxygen (reaction 3b) and KMnO₄ (reaction 2a) gave different ratios of the oxidation products 4 and 5.

The ONSH reaction of nitrobenzene with 1⁻ and KMnO₄ was successfully extended to a variety of substituted nitrobenzene derivatives. The results of these experiments, carried out

(1⁻ + 2a) + O₂ $\xrightarrow[\text{then NH}_4\text{Cl}]{\substack{\text{NH}_3\text{liq.}\\-70\ ^\circ\text{C, 2 min.}}}$ 1 • 2a • 3a + 4   (a)
   73 %   91 %   8 %   16 %

1⁻ + O₂ $\xrightarrow[\text{then NH}_4\text{Cl}]{\substack{\text{NH}_3\text{liq.}\\-70\ ^\circ\text{C, 2 min.}}}$ 1 + 4 + 5   (b)
   2 %   74 %   24 %

Scheme 3. Attempted oxidative nucleophilic substitution of hydrogen in nitrobenzene with oxygen as the oxidant.

under the standard conditions, are presented in Table 1. Although the ONSH reaction of **1** with a variety of nitroarenes usually gave the corresponding products **3a–r** in high yields, there were some nitroarenes that did not react satisfactorily. It was important to learn which step of this process was responsible for the low yields of the ONSH products in these cases. In order to answer this question we estimated the concentration of the corresponding σ^H adducts **12⁻** by means of the reaction with MeI (see equation 2d). Usually a high concentration of the σ^H adducts resulted in high yields of the ONSH products. There were, however, a few cases where yields of the ONSH products were low in spite of practically quantitative conversion of the carbanion and nitroarene into σ^H adducts. This can undoubtedly be explained by the substituents in the aromatic rings hindering the oxidation, but not the addition process.

This lack of correlation between formation of the σ^H adducts and yields of the ONSH products should provide some information concerning the parameters affecting the oxidation process. For a simpler analysis of this correlation, we used a semiquantitative coefficient r, which is defined as the yield of ONSH product divided by amount of σ^H adduct determined by reaction with MeI (Table 1). Values of r close to 1 indicate an effective oxidation; lower values indicate that the substituents at the aromatic ring inhibit the oxidation. This inhibitory effect, particularly in the case of the nitrobenzenes with 3-I, 3,5-Cl$_2$, and 3-I,5-F substituents (**2i**, **2l**, **2n** etc.), appears to be steric in origin. Electronic effects can apparently be excluded, because the presence of one Cl substituent in the ring does not affect the oxidation process of the corresponding σ^H adducts (r(2-Cl) = 0.79, r(3-Cl) = 0.93); thus, the electronic effect of the second Cl should also be negligible.

A very important feature of the reaction described here is its *para* selectivity. In all the nitrobenzene derivatives studied (Table 1), we did not observe any formation of the *ortho* ONSH products. Moreover, when nitrobenzene derivatives containing substituents in the *para* positions were used (e.g. *p*-chloronitrobenzene and *p*-nitrobiphenyl), no ONSH products were formed under the standard conditions; the nitroarene was recovered and the carbanion oxidized according to reaction 2a. In *p*-chloronitrobenzene, the S$_N$Ar substitution of the halogen was observed to a small extent. On the other hand, this was the major process with *p*-fluoronitrobenzene. This selective *para* substitution and the absence of ONSH products in the *ortho* position can be rationalized by steric hindrance in the addition of the bulky, tertiary carbanions at the *ortho* position and steric as well as electrostatic hindrance in the oxidation of the *ortho* σ^H adduct.

The reaction with MeI provides important information about the equilibrium in Scheme 1 and about the presence of the σ^H adducts. However, it is only an indirect indicator, measuring the amount of free carbanion **1⁻** in the reaction mixture; the remaining **1⁻** is assumed to have formed the σ^H adduct. An independent, direct measure of the σ^H adduct concentration, based on its reaction with an electrophile, would be of great interest. Moreover, such a reaction could also be of substantial value in synthesis. Trimethylsilyl chloride was expected to be a suitable electrophile, because of its "oxygenophilicity"; however, for ob-

vious reasons it is not compatible with liquid ammonia. Therefore, the reaction of **12⁻a** with Me$_3$SiCl was attempted in a THF/DMF mixture at −70 °C. It was first shown that **1⁻** generated under these conditions reacted almost quantitatively with methyl iodide. The methylation could therefore be used in this solvent too to measure the extent of σ^H adduct formation. Thus, nitrobenzene (**2a**) was added to a solution of **1⁻** in THF/DMF at −70 °C; methylation of **1⁻** in this reaction mixture occurred to a negligible extent, indicating high conversion of **1⁻** into the σ^H adduct **12⁻a**. Addition of Me$_3$SiCl to the system **1⁻** and **2a** in THF/DMF at −70 °C resulted in a light green coloration of the mixture, indicating formation of a nitroso compound. Indeed standard workup gave **7a** in high yield (Scheme 4). The probable reaction pathway is shown in Scheme 4.
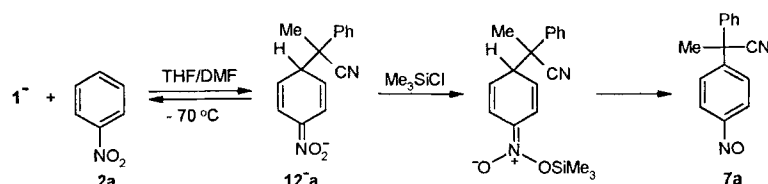
Scheme 4. Reaction of **12⁻a** with (CH$_3$)$_3$SiCl.

The formation of substituted nitroso compounds by silylation of the **12⁻** σ^H adducts seems to be a general method for detecting nitroarenes entering the ONSH process. The procedure was succesfully tested on three nitroarenes **2a**, **2e**, and **2j**, but failed for **2l**. In the case of **2a**, **2e**, and **2j**, the starting nitroarenes were almost completely consumed. However, the resulting nitrosoarenes were of limited stability and underwent partial or complete disproportionation during isolation and purification, to form the corresponding nitroarenes and azoxy compounds (Scheme 5).
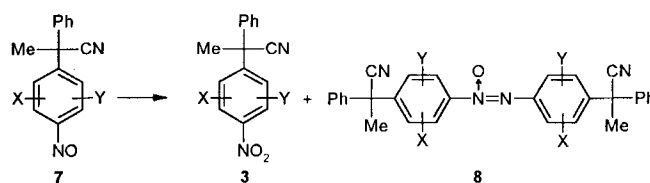
Scheme 5. Disproportionation of nitrosoarenes **2a**, **2e**, and **2j**.

Only in two cases (**7a**, **7e**) were we able to isolate the nitroso compounds and characterize them partially by means of ^{14}N NMR and mass spectrometry. 3,5-Dichloronitrobenzene (**2l**) did not show any reaction. When we used highly electrophilic 3,5-difluoronitrobenzene (**2j**), decomposition of the nitroso compound was so fast that the only products isolated after workup were **3j** and **8j**.

As already mentioned, some σ^H adducts resist oxidation with KMnO$_4$ in liquid ammonia, although they are formed practically quantitatively, as indicated by tests with MeI; for example, the value of r for 3,5-dichloronitrobenzene (**3l**) is 0.01. The reasons for this behavior are not yet clear. Attempts to convert this adduct into the nitroso compound by reaction with Me$_3$SiCl in THF/DMF mixture also failed. It is known that some nucleophile–nitroarene σ^H adducts can be oxidized by

addition of bromine followed by elimination of HBr.[9] We examined this method of oxidation for the σ^H adducts of 1^- with **2a**, **2i**, and **2l**. For obvious reasons, this reaction could not be conducted in liquid ammonia. It was therefore attempted in THF/DMF at $-70\,^\circ$C. The yields obtained were good for **2a** (79%) and satisfactory for **2i** (37%). In the case of **2l** this reaction was unsuccessful—the nitro compound and **1** were regenerated practically quantitatively. Taking into account that the σ^H adducts of these nitroarenes are generated almost quantitatively, as determined by the reaction with MeI, the substituents in the aromatic ring apparently hinder the oxidation process.

It should be stressed that the failure of the ONSH of **2l** with $KMnO_4$ and Br_2 as oxidants and also the failure of silylation of 12^-l are due to the resistance of this σ^H adduct towards reaction with these reagents. Complete addition of 1^- to **2l** giving 12^-l has been confirmed by the methylation test and supported by full recovery of **1** upon quenching of the reaction mixtures after treatment of 12^-l with $KMnO_4$ in liquid ammonia and bromine or Me_3SiCl in THF/DMF. Free or weakly associated 1^- would have reacted rapidly with these reagents.

Experimental Section

General: Melting points are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1640 spectrophotometer. Elemental analyses were performed by the Microanalysis Laboratory of IChO PAN. High-resolution EI mass spectra were obtained on an AMD 604 mass spectrometer. ^{1}H NMR spectra were recorded on a Varian Gemini (200 MHz) spectrometer with either the solvent reference or TMS as internal standards. ^{14}N NMR were recorded on a Bruker AMKS (500 MHz) spectrometer. GC analyses were carried out on a Shimadzu GC-14A instrument with a fused silica capillary column (0.25 mm × 25 m, SE-52-DF-0.25 permabond). Thin-layer chromatography (TLC) was carried out on aluminum sheets precoated with silica gel 60F (Merck 5554). The plates were inspected by UV light. Column chromatography was carried out on silica gel 60F (Merck, 230–400 mesh). Chemicals were commercial from either Aldrich or Fluka and used as received with the exception of 3,5-dichloronitrobenzene, which was prepared from 2,6-dichloro-4-nitroaniline.[10] Solvents were dried (DMF with CaH_2, THF with sodium benzophenone ketyl) according to procedures described in the literature.[11] All reactions were conducted under argon. The yields are of isolated products without optimization.

1) General Procedure for ONSH in Nitroarenes 2a–r: 2-Phenylpropionitrile (**1**) (197 mg, 1.5 mmol) was added dropwise, within 30 s to a suspension of sodium amide freshly prepared from sodium (38 mg, 1.65 mmol) in liquid ammonia (ca. 25 mL) at $-70\,^\circ$C. After one minute nitroarene **2a–r** (1.5 mmol) dissolved in DMF (1 mL) was added dropwise at such a rate that the temperature did not exceed $-70\,^\circ$C. The reaction mixture was stirred for 2 min, after which time solid potassium permanganate (237 mg, 1.5 mmol) was added in one portion. The reaction mixture was stirred for 2 min and quenched with solid ammonium chloride (803 mg, 15 mmol). The ammonia was evaporated. Extraction with CH_2Cl_2, washing with water and brine, drying with $MgSO_4$, and chromatography yielded the crude product, which was recrystallized from EtOH affording the pure nitro compound **3a–r**.

3a: M.p. 78 79 °C (Lit. 76 °C);[6] ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 2.22$ (s, 3H; CH$_3$), 7.33–7.54 (m, 5H; Ph), 7.75 (m, 2H; AA′ of AA′XX′ system), 8.29 (m, 2H; XX′ of AA′XX′ system); IR (KBr): $\tilde{v} = 2238$ (CN), 1522 and 1348 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 252 (53) [M^+], 237 (100) [$M^+ -$ CH$_3$], 206 (4) [$M^+ -$ NO$_2$], 191 (43) [$M^+ -$ NO$_2$ – CH$_3$]; $C_{15}H_{12}N_2O_2$ (252.27): calcd C 71.42, H 4.79, N 11.10; found C 71.37, H 4.65, N 11.02.

3b: Oil; ^{1}H NMR (200 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 2.18$ (s, 3H; CH$_3$), 7.36–7.49 (m, 5H; Ph), 7.45–7.52 (ddd, ^4J(H,H) = 2.1 Hz, ^5J(F,H) =

1.0 Hz, 1H; H-9), 7.68 (dd, ^3J(F,H) = 12.4 Hz, ^4J(H,H) = 2.1 Hz, 1H; H-5), 8.22 (t, ^4J(F,H) = 8 Hz, 1H; H-8); IR (Nujol): $\tilde{v} = 2239$ (CN), 1538 and 1346 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 270 (53) [M^+], 255 (100) [$M^+ -$ CH$_3$], 224 (5) [$C_{15}H_{11}N_1F_1^+$], 209 (73) [$C_{14}H_8N_1F_1^+$]; $C_{15}H_{11}N_2O_2F_1$ (270.26): calcd C 66.66, H 4.10, N 10.37; found C 66.64, H 4.03, N 10.34.

3c: Oil; ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 2.24$ (s, 3H; CH$_3$), 7.35–7.47 (m, 5H; Ph), 7.96–8.06 (q, ^3J(H,H) = 8.6 Hz, ^4J(F,H) = 8 Hz, 1H; H-9), 8.01–8.09 (dd, ^3J(F,H) = 10.9 Hz, ^4J(H,H) = 2.3 Hz, 1H; H-6), 8.21–8.28 (ddd, ^3J(H,H) = 8.6 Hz, ^4J(H,H) = 2.3 Hz, ^5J(F,H) = 1.0 Hz, 1H; H-8); IR (Nujol): $\tilde{v} = 2241$ (CN), 1532 and 1353 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 270 (53) [M^+], 255 (100) [$M^+ -$ CH$_3$], 224 (7) [$C_{15}H_{11}N_1F_1^+$], 209 (39) [$C_{14}H_8N_1F_1^+$]; $C_{15}H_{11}N_2O_2F_1$ (270.26): calcd C 66.66, H 4.10, N 10.37; found C 66.59, H 4.04, N 10.31.

3d: M.p. 49–51 °C (Lit. 51 °C);[6] ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 2.24$ (s, 3H; CH$_3$), 7.35–7.58 (m, 5H; Ph), 7.67 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.9 Hz, 1H; H-9), 7.76 (d, ^4J(H,H) = 1.9 Hz, 1H; H-5), 8.10 (d, ^3J(H,H) = 8.4 Hz, 1H; H-8); IR (KBr): $\tilde{v} = 2240$ (CN), 1525 and 1345 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 286 (57) [M^+], 271 (97) [$M^+ -$ CH$_3$], 225 (18) [$M^+ -$ CH$_3$ – NO$_2$], 190 (100) [$C_{14}H_8N_1^+$]; $C_{15}H_{11}N_2O_2Cl_1$ (286.74): calcd C 62.93, H 3.88, N 9.79, Cl 12.22; found C 62.83, H 3.69, N 9.79, Cl 12.39.

3e: M.p. 89–90 °C (Lit. 92 °C);[6] ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 2.24$ (s, 3H; CH$_3$), 7.26–7.46 (m, 5H; Ph), 8.19 (d, ^3J(H,H) = 8.8 Hz, 1H; H-9), 8.28 (d, ^4J(H,H) = 2.4 Hz, 1H; H-6), 8.38 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 2.4 Hz, 1H; H-8); IR (KBr): $\tilde{v} = 2240$ (CN), 1517 and 1348 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 286 (82) [M^+], 271 (100) [$M^+ -$ CH$_3$], 251 (57) [$M^+ -$ Cl], 190 (93) [$C_{14}H_8N_1^+$]; $C_{15}H_{11}N_2O_2Cl_1$ (286.74): calcd C 62.93, H 3.88, N 9.79, Cl 12.22; found C 62.84, H 3.79, N 9.86, Cl 12.08.

3f: M.p. 82–84 °C (Lit. 85 °C);[6] ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 2.25$ (s, 3H; CH$_3$), 7.36–7.58 (m, 5H; Ph), 7.71 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.1 Hz, 1H; H-9), 7.92 (d, ^4J(H,H) = 2.1 Hz, 1H; H-5), 8.04 (d, ^3J(H,H) = 8.5 Hz, 1H; H-8); IR (KBr): $\tilde{v} = 2242$ (CN), 1523 and 1342 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 332 (37) and 330 (37) [M^+], 317 (61) and 315 (61) [$M^+ -$ CH$_3$], 236 (57) [$M^+ -$ CH$_3$ – Br], 190 (100) [$C_{14}H_8N_1^+$]; $C_{15}H_{11}N_2O_2Br_1$ (331.17): calcd C 54.40, H 3.35, N 8.46, Br 24.13; found C 54.41, H 3.19, N 8.43, Br 24.04.

3g: M.p. 111–112 °C; ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 2.26$ (s, 3H; CH$_3$), 7.21–7.48 (m, 5H; Ph), 8.17 (d, ^3J(H,H) = 8.8 Hz, 1H; H-9), 8.46 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 2.5 Hz, 1H; H-8), 8.76 (d, ^4J(H,H) = 2.5 Hz, 1H; H-6); IR (KBr): $\tilde{v} = 2238$ (CN), 1526 and 1346 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 332 (72) and 330 (73) [M^+], 317 (28) and 315 (28) [$M^+ -$ CH$_3$], 251 (90) [$M^+ -$ Br], 236 (65) [$M^+ -$ CH$_3$ – Br], 205 (86) [$M^+ -$ Br-NO$_2$], 190 (20) [$C_{14}H_8N_1^+$]; $C_{15}H_{11}N_2O_2Br_1$ (331.17): calcd C 54.40, H 3.35, N 8.46, Br 24.13; found C 54.49, H 3.27, N 8.42, Br 24.25.

3h: M.p. 107–108 °C; ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 2.23$ (s, 3H; CH$_3$), 7.35–7.58 (m, 5H; Ph), 7.71 (dd, ^3J(H,H) = 8.5 Hz, ^4J(H,H) = 2.1 Hz, 1H; H-9), 7.98 (d, ^4J(H,H) = 2.1 Hz, 1H; H-5), 8.16 (d, ^3J(H,H) = 8.5 Hz, 1H; H-8); IR (KBr): $\tilde{v} = 2244$ (CN), 1522 and 1340 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 378 (100) [M^+], 363 (76) [$M^+ -$ CH$_3$], 237 (5) [$C_{14}H_9N_2O_2^+$], 190 (37) [$C_{14}H_8N_1^+$]; $C_{15}H_{11}N_2O_2I_1$ (378.17): calcd C 47.64, H 2.93, N 7.41, I 33.56; found C 47.83, H 2.86, N 7.36, I 33.42.

3i: M.p. 117–118 °C; ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 2.26$ (s, 3H; CH$_3$), 7.21–7.48 (m, 5H; Ph), 8.17 (d, ^3J(H,H) = 8.8 Hz, 1H; H-9), 8.46 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 2.5 Hz, 1H; H-8), 8.76 (d, ^4J(H,H) = 2.5 Hz, 1H; H-6); IR (KBr): $\tilde{v} = 2238$ (CN), 1523 and 1349 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 378 (100) [M^+], 251 (76) [$M^+ -$ I], 236 (18) [$M^+ -$ I – CH$_3$], 205 (72) [$M^+ -$ I – NO$_2$], 190 (56) [$C_{14}H_8N_1^+$]; $C_{15}H_{11}N_2O_2I_1$ (378.17): calcd C 47.64, H 2.93, N 7.41, I 33.56; found C 47.68, H 2.88, N 7.40, I 33.66.

3j: Oil; ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C, TMS): $\delta = 2.30$ (t, ^5J(F,H) = 3.0 Hz, 3H; CH$_3$), 7.34–7.54 (m, 5H; Ph), 8.01 (m, 2H; AA′ of AA′XX′ system); IR (KBr): $\tilde{v} = 2243$ (CN), 1538 and 1351 cm^{-1} (NO$_2$); MS

(70 eV, EI): m/z (%): 288 (100) $[M^+]$, 273 (100) $[M^+ - CH_3]$, 242 (6) $[M^+ - NO_2]$, 227 (20) $[C_{14}H_7N_1F_2^+]$, 215 (6) $[C_{14}H_9F_2^+]$; $C_{15}H_{10}N_2O_2F_2$ (288.25): calcd C 62.50, H 3.50, N 9.72; found C 62. 36, H 3.28, N 9.68.

3k: M.p. 145–147 °C; ^{1}H NMR (200 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta =$ 2.27 (s, 3H; CH$_3$), 7.32–7.49 (m, 5H; Ph), 8.18 (s, 1H; H-9), 8.19 (s, 1H; H-6); IR (KBr): $\tilde{v} =$ 2240 (CN), 1521 and 1349 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 320 (65) $[M^+]$, 305 (41) $[M^+ - CH_3]$, 285 (100) $[M^+ - Cl]$, 239 (29) $[M^+ - Cl - NO_2]$, 224 (78) $[C_{14}H_7N_1Cl_1^+]$; $C_{15}H_{10}N_2O_2Cl_2$ (321.16): calcd C 56.10, H 3.14, N 8.72, Cl 22.08; found C 56.11, H 3.02, N 8.66, Cl 22.03.

3l: Yield of 1% estimated by GC/MS; m/z (%): 320 (51) $[M^+]$, 305 (46) $[M^+ - CH_3]$, 285 (98) $[M^+ - Cl]$, 258 (68) $[M^+ - Cl - HCN]$, 239 (33) $[M^+ - Cl - NO_2]$, 224 (100) $[C_{14}H_7N_1Cl_1^+]$.

3m: M.p. 165–166 °C; ^{1}H NMR (200 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta =$ 2.28 (s, 3H; CH$_3$), 7.30–7.48 (m, 5H; Ph), 8.30 (s, 1H; H-9), 8.31 (s, 1H; H-6); IR (KBr): $\tilde{v} =$ 2237 (CN), 1519 and 1338 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 408 (91) $[M^+]$, 393 (17) $[M^+ - CH_3]$, 331 (100) and 329 (99) $[M^+ - Br]$, 285 (58) and 283 (58) $[M^+ - Br - NO_2]$, 250 (55) $[M^+ - 2Br]$, 204 (55) $[M^+ - 2Br - NO_2]$; $C_{15}H_{10}N_2O_2Br_2$ (410.07): calcd C 43.94, H 2.46, N 6.83, Br 38.97; found C 44.06, H 2.33, N 6.85, Br 38.85.

3n: Oil; ^{1}H NMR (200 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta =$ 2.33 (s, 3H; CH$_3$), 7.27–7.52 (m, 5H; Ph), 8.24 (dd, $^3J(F,H) =$ 12.7 Hz, $^4J(H,H) =$ 2.4 Hz, 1H; H-6), 8.63 (dd, $^4J(H,H) =$ 2.4 Hz, $^5J(F,H) =$ 1.4 Hz, 1H; H-8); IR (KBr): $\tilde{v} =$ 2236 (CN), 1531 and 1347 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 396 (100) $[M^+]$, 269 (22) $[M^+ - I]$, 254 (22) $[M^+ - I - CH_3]$, 242 (48) $[M^+ - I - HCN]$, 223 (47) $[M^+ - I - NO_2]$, 208 (55) $[M^+ - I - NO_2 - CH_3]$; HRMS (EI) m/z calcd for $C_{15}H_{10}N_2O_2F_1I_1$: 395.977108, found: 395.977989.

3o: M.p. 107–109 °C (Lit. 109 °C);[16] ^{1}H NMR (200 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta =$ 2.22 (s, 3H; CH$_3$), 3.99 (s, 3H; OCH$_3$), 7.16 (dd, $^3J(H,H) =$ 8.5 Hz, $^4J(H,H) =$ 2.0 Hz, 1H; H-9), 7.39 (d, $^4J(H,H) =$ 2.0 Hz, 1H; H-5), 7.34–7.55 (m, 5H; Ph), 7.89 (d, $^3J(H,H) =$ 8.5 Hz, 1H; H-8); IR (KBr): $\tilde{v} =$ 2239 (CN), 1513 and 1344 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 282 (100) $[M^+]$, 267 (41) $[M^+ - CH_3]$, 221 (76) $[C_{15}H_{11}N_1O_1^+]$; $C_{16}H_{14}N_2O_3$ (282.30): calcd C 68.08, H 5.00, N 9.92; found C 68. 06, H 5.02, N 9.90.

3p: M.p. 117–118 °C; ^{1}H NMR (200 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta =$ 2.15 (s, 3H; CH$_3$), 3.80 (s, 3H; OCH$_3$), 7.30–7.41 (m, 5H; Ph), 7.80–8.01 (m, 3H; Ar); IR (KBr): $\tilde{v} =$ 2240 (CN), 1520 and 1346 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 282 (37) $[M^+]$, 267 (41) $[M^+ - CH_3]$, 91 (100) $[C_7H_7^+]$; $C_{16}H_{14}N_2O_3$ (282.30): calcd C 68.08, H 5.00, N 9.92; found C 68. 05, H 4.93, N 9.87.

3r: M.p. 124–125 °C; ^{1}H NMR (200 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta =$ 2.34 (s, 3H; CH$_3$), 7.35–7.52 (m, 5H; Ph), 8.30–8.34 (m, 1H; H-9), 8.66–8.74 (m, 2H; Ar); IR (KBr): $\tilde{v} =$ 2235 (CN), 1529 and 1354 cm^{-1} (NO$_2$); MS (70 eV, EI): m/z (%): 277 (54) $[M^+]$, 262 (100) $[M^+ - CH_3]$, 216 (38) $[M^+ - CH_3 - NO_2]$; $C_{16}H_{11}N_3O_2$ (277.28): calcd C 69.31, H 4.00, N 15.15; found C 69. 36, H 3.85, N 15.27.

2) Experimental Procedure for Reactions Shown in Scheme 2:
a) Oxidation of 1$^-$ with KMnO$_4$: KMnO$_4$ (237 mg, 1.5 mmol) was added in one portion to a solution of 1$^-$ (197 mg, 1.5 mmol) in liquid ammonia, prepared as described in procedure 1. After 2 min the mixture was quenched with NH$_4$Cl, the ammonia evaporated, and the residue analyzed by GC/MS using biphenyl as an internal standard: **4** (20%), **5** (80%), **1** (traces).

b) Reaction of 1$^-$ with equimolar mixture of 2a and KMnO$_4$: A solution of 1$^-$ (197 mg, 1.5 mmol) in liquid ammonia, prepared as described in procedure 1, was added in one portion to a solution of KMnO$_4$ (237 mg, 1.5 mmol) and **2a** (185 mg, 1.5 mmol) in liquid ammonia (ca. 25 mL) at −70 °C. After 2 min the mixture was quenched with NH$_4$Cl, ammonia evaporated, and the residue analyzed by GC/MS using biphenyl as an internal standard: **2a** (90%), **3a** (10%), **4** (18%), **5** (65%).

c) Reaction of 1$^-$ with MeI: MeI (213 mg, 1.5 mmol) was added in one portion to a solution of 1$^-$ (197 mg, 1.5 mmol) in liquid ammonia, prepared

as described in procedure 1. After 2 min the mixture was quenched with NH$_4$Cl, ammonia evaporated, and the residue analyzed by GC using biphenyl as an internal standard: **1** (traces), **6** (99%).

d) Reaction of MeI with equimolar mixture of 2a and 1$^-$: MeI (213 mg, 1.5 mmol) was added in one portion to a solution of 1$^-$ (197 mg, 1.5 mmol), prepared as described in procedure 1, and **2a** (185 mg, 1.5 mmol) in liquid ammonia. After 2 min the mixture was quenched with NH$_4$Cl, the ammonia evaporated, and the residue analyzed by GC using biphenyl as an internal standard: **2a** (98%), **1** (99%), **6** (1%).

e) Reaction of 1$^-$ with equimolar mixture of 2a and MeI: A solution of 1$^-$ (197 mg, 1.5 mmol) in liquid ammonia, prepared as described in procedure 1, was added in one portion to a solution of MeI (213 mg, 1.5 mmol) and **2a** (185 mg, 1.5 mmol) in liquid ammonia (ca. 25 mL) at −70 °C. After 2 min the mixture was quenched with NH$_4$Cl, the ammonia evaporated, and the residue analyzed by GC using biphenyl as an internal standard: **1** (48%), **2a** (99%), **6** (52%).

f) Reaction of 1$^-$ with equimolar mixture of KMnO$_4$ and MeI: A solution of 1$^-$ (197 mg, 1.5 mmol) in liquid ammonia, prepared as described in procedure 1, was added in one portion to a solution of KMnO$_4$ (237 mg, 1.5 mmol) and MeI (213 mg, 1.5 mmol) in liquid ammonia (ca. 25 mL) at −70 °C. After 2 min the mixture was quenched with NH$_4$Cl, the ammonia evaporated, and the residue analyzed by GC/MS using biphenyl as an internal standard: **4** (17%), **5** (73%), **6** (10%).

g) Reaction of KMnO$_4$ with equimolar mixture of 1$^-$ and σ^H adduct 12$^-$a: KMnO$_4$ (237 mg, 1.5 mmol) was added in one portion to a solution of 1$^-$ (394 mg, 3.0 mmol), prepared as described in procedure 1, and **2a** (185 mg, 1.5 mmol) in liquid ammonia. After 2 min the mixture was quenched with NH$_4$Cl, the ammonia evaporated, and the residue analyzed by GC using biphenyl as an internal standard: **1** (35%), **2a** (10%), **3a** (90%), **4** and **5** (20%).

3) Experimental Procedure for Reactions Shown in Scheme 3:
a) Reaction of equimolar mixture of 1$^-$ and 2a with oxygen: A strong stream of oxygen was bubbled through a solution of 1$^-$ (197 mg, 1.5 mmol), prepared as described in procedure 1, and **2a** (185 mg, 1.5 mmol) in liquid ammonia. After 2 min the mixture was quenched with NH$_4$Cl, the ammonia evaporated, and the residue analyzed by GC using biphenyl as an internal standard: **1** (73%), **2a** (91%), **3a** (8%), **4** (16%).

b) Reaction of 1$^-$ with oxygen: A strong stream of oxygen was bubbled through a solution of 1$^-$ (197 mg, 1.5 mmol) in liquid ammonia, prepared as described in procedure 1. After 2 min the mixture was quenched with NH$_4$Cl, the ammonia evaporated, and the residue analyzed by GC using biphenyl as an internal standard: **1** (2%), **4** (74%), **5** (24%).

4) Reaction of Anionic σ^H Adducts 12$^-$a, 12$^-$e, and 12$^-$j with Me$_3$SiCl: A solution of 2-phenylpropionitrile (197 mg, 1.5 mmol) and nitroarene (1.5 mmol) in DMF (1 mL) was added dropwise to a solution of tBuOK (185 mg, 1.65 mmol) in anhydrous THF (20 mL) at −70 °C under argon. After completion of the addition (1 min), the reaction mixture was allowed to stir for 2 min, and the orange solution was treated with Me$_3$SiCl (0.5 mL). The resulting clear solution was stirred at −70 °C for 0.5–1 h, and HCl (10%, 10 mL) was then added. Extraction with CH$_2$Cl$_2$, washing with KHCO$_3$ (5%), water, and brine, and drying with MgSO$_4$ yielded the crude product, which was purified by flash chromatography affording the light green oil.

7a: Yield 319 mg (90%); green oil; ^{14}N NMR (500 MHz, $[D_6]$acetone, 25 °C, CH$_3$NO$_2$): $\delta = -132$ (CN and NO$_{dimer}$), 527 (NO$_{monomer}$); MS (70 eV, EI): m/z (%): 236 (100) $[M^+]$, 221 (9) $[M^+ - CH_3]$, 206 (38) $[M^+ - NO]$, 190 (52) $[C_{14}H_8N_1^+]$.

7e: Yield 285 mg (70%); green oil; ^{14}N NMR (500 MHz, $[D_6]$acetone, 25 °C, CH$_3$NO$_2$): $\delta = -130$ (CN and NO$_{dimer}$), 527 (NO$_{monomer}$); MS (70 eV, EI): m/z (%): 270 (100) $[M^+]$, 255 (22) $[M^+ - CH_3]$, 240 (22) $[M^+ - NO]$, 225 (12) $[M^+ - NO - CH_3]$, 205 (34) $[M^+ - NO - Cl]$, 190 (71) $[C_{14}H_8N_1^+]$.

3j: Yield 86 mg (20%); **8j**: Yield 135 mg (34%); Oil; ^{1}H NMR (200 MHz, $[D_6]$acetone, 25 °C, TMS): $\delta =$ 2.20–2.30 (m, 6H; CH$_3$), 7.35–7.51 (m,

10H; Ph), 7.75–7.88 (m, 4H; AA' of AA'XX' system), 7.90–8.03 (m, 4H; AA' of AA'XX' system); IR (KBr): $\tilde{v}$ = 2238 (CN), 1480 cm^{-1} (N=N); MS (70 eV, EI): m/z (%): 528 (97) [M^+], 513 (57) [M^+ − CH$_3$], 512 (51) [M^+ − O], 242 (100) [M^+ − O − N$_2$], 227 (40) [C$_{14}$H$_7$N$_1$F$_2^+$]; C$_{30}$H$_{20}$N$_4$O$_1$F$_4$ (528.16): calcd C 68.18, H 3.81, N 10.60; found C 68.12, H 3.84, N 10.44.

5) Products of Decomposition of Nitroso Compounds 7a and 7e:

3a: Yield 123 mg (36%); **8a:** Yield 126 mg (41%); oil; ^{1}H NMR (200 MHz, [D$_6$]acetone, 25 °C, TMS): δ = 2.18 (s, 3H; CH$_3$), 2.20 (s, 3H; CH$_3$), 7.31–7.55 (m, 10H; Ph), 7.56–7.72 (m, 4H; AA' portions of AA'XX' systems), 8.14–8.40 (m, 4H; XX' portions of AA'XX' systems); IR (KBr): $\tilde{v}$ = 2238 (CN), 1464 cm^{-1} (N=N); MS (70 eV, EI): m/z (%): 456 (39) [M^+], 440 (12) [M^+ − O], 206 (100) [M^+ − O − N$_2$], 190 (23) [C$_{14}$H$_8$N$_1^+$]; C$_{30}$H$_{24}$N$_4$O$_1$ (456.55): calcd C 78.92, H 5.30, N 12.27; found C 78.83, 5.21 H, 12.19 N.

3e: Yield 70 mg (23%); **8e:** Yield 177 mg (64%); Oil; ^{1}H NMR (200 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 2.19 (s, 3H; CH$_3$), 2.22 (s, 3H; CH$_3$), 7.25–7.50 (m, 12H; aromatic protons), 8.00–8.50 (m, 4H; aromatic protons); IR (KBr): $\tilde{v}$ = 2236 (CN), 1460 cm^{-1} (N=N); MS (70 eV, EI): m/z (%): 524 (76) [M^+], 508 (23) [M^+ − O], 489 (40) [M^+ − Cl], 240 (100) [M^+ − O − N$_2$], 190 (35) [C$_{14}$H$_8$N$_1^+$]; C$_{30}$H$_{22}$N$_4$O$_1$Cl$_2$ (525.44): calcd C 68.58, H 4.22, N 10.66, Cl 13.49; found C 68.45, H 4.05, N 10.71, Cl 13.48.

6) Reaction of Anionic σ^H Adducts with Bromine—Syntheses of Nitro Compounds 3a and 3i:

A solution of 2-phenylpropionitrile (197 mg, 1.5 mmol) and nitroarene (1.5 mmol) in DMF (1 mL) was added dropwise to a solution of tBuOK (185 mg, 1.65 mmol) in anhydrous THF (20 mL) at −70 °C under argon. After completion of the addition (1 min), the reaction mixture was stirred for 2 min and treated with bromine (0.4 mL, excess). The resulting deep orange solution was stirred at −70 °C for 40 min, and Et$_3$N (1 mL) was then added. After 20 min the solution was treated with aqueous NaHSO$_3$ (5%). Extraction with CH$_2$Cl$_2$, washing with KHCO$_3$ (5%), water, and brine, and drying with MgSO$_4$ yielded the crude product, which was recrystallized from EtOH affording the pure nitrocompound **3a** (79%) or **3i** (37%).

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