Polar Effects in Free Radical Reactions. Homolytic Aromatic Amination by the Amino Radical Cation, $\bullet^{+}NH_3$: Reactivity and Selectivity

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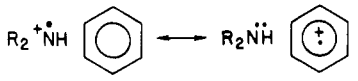
Small amounts of Fe(II) salt initiate redox chains with hydroxyamino-*O*-sulfonic acid (HSA) and aromatic compounds leading to the amination of the aromatic ring. The positional and substrate selectivity with a variety of substituted benzenes show the important role of the electrophilic character of the radical $\cdot^{+}NH_3$. Hammett relationships with σ and σ^{+} are roughly observed. The lower sensitivity to polar effects of the radical $\cdot^{+}NH_3$ compared with $(CH_3)_2{}^{+}\dot{N}H$ is explained by the different reaction enthalpies. The different positional selectivity obtained with anisole and the redox system $^{+}NH_3OH$/Ti(III) is discussed.

The amination of aromatic compounds by *N,N*-dialkyl, $R_2{}^{+}\dot{N}H$, and *N*-monoalkyl, $R^{+}\dot{N}H_2$, amino radical cations from *N*-alkylchloramines in acidic medium is particularly interesting for the synthetic and theoretical involvements.[1] The exceptional positional and substrate selectivity, observed with many aromatic substrates has been ascribed to the polar effects connected with the strong electrophilic character of the alkylamino radical cations and with a charge-transfer character of the transition state[1] (eq 1).



(1)

The behavior of the simple amino radical cation, $\cdot^{+}NH_3$, for which a similar trend would be expected, has been less investigated. Unfortunately the use of the *N*-chloramine, NH_2Cl, in acidic medium in order to have a homogeneous comparison proved to be unsuitable.

Years ago two different radical sources were investigated for the aromatic amination by $\cdot^{+}NH_3$, the redox couples $^{+}NH_3OH$/Ti(III)[2] (eq 2) and $^{+}NH_3OSO_3^{-}$/Fe(II)[3] (eq 3).

$$^{+}NH_3OH + Ti^{3+} + H^{+} \rightarrow \cdot^{+}NH_3 + Ti^{4+} + H_2O \quad (2)$$

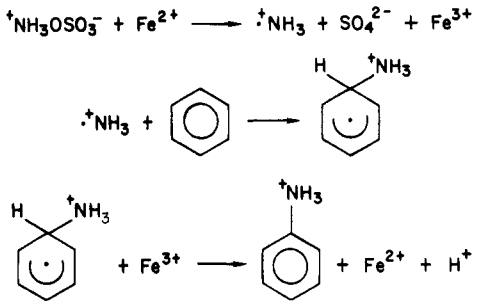
$$^{+}NH_3OSO_3^{-} + Fe^{2+} \rightarrow \cdot^{+}NH_3 + Fe^{3+} + SO_4^{2-} \quad (3)$$

Reaction 2 has, however, shown a limited range of application with activated aromatics (methoxybenzenes), whereas with unactivated aromatic compounds, such as benzene, the addition of the amino radical to the aromatic ring is not followed by the rearomatization of the intermediate aminocyclohexadienyl radical adduct.

Reaction 3 has shown a larger range of application, but, under the reaction conditions used, the yields of amination were poor, with the exception of anisole; thus an extensive investigation was not carried out.

Recently[4] we have shown that the reaction 3 can be used with good efficiency to generate nucleophilic carbon-centered radicals useful for the substitution of heteroaromatic bases. We have therefore reconsidered the reaction 3 also for the aromatic amination finding conditions in which the yields, considerably increased in comparison with previous results,[3] justified a deeper investigation.

Scheme I



Moreover we have reconsidered also the reaction 2 in the amination of anisole because previous studies had shown different positional selectivities with the two different sources[3] (eq 2 and 3).

Results and Discussion

Previous investigations[3] with hydroxylamine-*O*-sulfonic acid (HSA) were carried out in methanol with stoichiometric amounts of ferrous salt. Moderate yields, based on HSA, were obtained with anisole, but yields were <10% with unactivated aromatics (benzene, toluene), and only traces of amination products were obtained with deactivated compounds (benzonitrile, ethyl benzoate, nitrobenzene).

The ortho–para orientation and the higher yields with anisole suggested that the electrophilic character of the radical $\cdot^{+}NH_3$ had to play an important role.

The recent results[4] of redox decomposition of HSA in methanol have shown the following competitive processes responsible for the low yields of attack of $\cdot^{+}NH_3$ to the aromatic ring:

i. hydrogen abstraction from methanol (eq 4)

$$\cdot^{+}NH_3 + CH_3OH \rightarrow {}^{+}NH_4 + \cdot CH_2OH \quad (4)$$

On the ground of polar and enthalpic factors, reaction must be very fast (close to the diffusion-controlled limit); the rate of hydrogen abstraction[5] by $(CH_3)_2{}^{+}\cdot NH$ from alkanes is $>10^6\ M^{-1}\ s^{-1}$, and the process is 20–25 kcal/mol more exothermic with $\cdot^{+}NH_3$ than with $(CH_3)_2{}^{+}\dot{N}H$:[6]

ii. reduction of $\cdot^{+}NH_3$ by Fe(II) salt (eq 5)

$$\cdot^{+}NH_3 + Fe^{2+} \rightarrow NH_3 + Fe^{3+} \quad (5)$$

iii. the hydrolysis[7] of HSA (eq 6)

$$^{+}NH_3OSO_3^{-} + H_2O \rightarrow {}^{+}NH_3OH\ HSO_4^{-} \quad (6)$$

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Table I. Isomer Distribution and Partial Rate Factors in the Amination of PhX Derivatives by $^{+}NH_3OSO_3^-$

X	isomer distribution			k_X/k_H	partial rate factors		
	o	m	p		o	m	p
OMe	28.5	1.7	69.8	4.80	4.10	0.24	20.10
Me	35.7	22.7	41.5	1.70	1.82	1.16	4.23
t-Bu	3.7	43.6	52.7	1.35	0.15	1.77	4.27
F	18.9	20.1	61.0	0.254	0.144	0.153	0.93
Cl	20.7	20.6	58.7	0.15	0.093	0.093	0.53
Br	18.0	23.5	58.5	0.196	0.106	0.138	0.69
COOEt	23.0	45.6	31.4	0.012	0.008	0.016	0.023
CN	9.8	51.6	38.6	0.011	0.003	0.017	0.025

Table II. Amination of PhX Derivatives by $^{+}NH_3OSO_3^-$, Ratio PhX:$^{+}NH_3^-$ 1:1 in AcOH:H_2O (2:1) and 3% of $FeSO_4 \cdot 7H_2O$ at 40 °C

X	convn,[a] %	X	convn,[a] %
OMe	60	Cl	24
Me	53	Br	30
H	56	COOEt	21
F	34	CN	5

[a] Yields, based on converted aromatic substrates, are >90%; diamines (2–4%) are the only byproducts of the reaction. The isomer distributions are substantially identical with those reported in Table I.

Hydroxylamine does not react with Fe(II) salts under the reaction conditions.

Thus in order to minimize these competitive processes we have used a solvent, acetic acid, less reactive toward $\cdot^{+}NH_3$ for polar reasons and the smallest amount of Fe(II) salt sufficient to sustain the redox chain already suggested in the previous studies[3] for the homolytic amination (Scheme I). Actually, under these conditions, satisfactory amination yields were obtained also with unactivated aromatic substrates, whereas with deactived substrates the yields were lower but still significant.

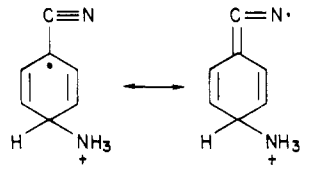
The remarkable fact is that the reaction takes place with a very small amount of Fe(II) salt (<1%). The yields of aromatic amination are practically unchanged in the range of 0.5–5% of Fe(II) salt, whereas the reaction rate increases with the amount of Fe(II) salt. At higher Fe(II)/HSA ratios the rate further increases, but the yields of amination decrease because the termination step (eq 5) of the chain of Scheme I becomes more important. In the absence of Fe(II) salt, under the same conditions, no amination reaction occurs.

Thus it would appear that the chains of Scheme I are rather long; the yields less than quantitative, based on HSA, must be therefore ascribed to the competitive eq 6 because the solvent cannot contribute to a redox chain. An alternate proposal that cannot be excluded is some hydroxylamine from hydrolysis (eq 6), reacts with HSA, producing a reducing species, such as NH=NH, which contributes to sustain the chain of the Scheme I by transforming Fe(III) to Fe(II) salt.

A quantitative study was carried out by using in all cases a ratio Fe(II)/HSA (1:33) in acetic acid:water (2:1) solution; the results are reported in Table I.

In Table II synthetic results are summarized.

The yields and the positional and substrate selectivity confirm the previous qualitative indications[3] that the electrophilic character of the radical $\cdot^{+}NH_3$ plays an important role in determining reactivity and selectivity. The meta:para ratio increases as the electron-withdrawing effect of the substituents increases, in agreement with the expected polar effect. The partial rate factors of the para positions, however, are always higher than those of the meta positions, even with benzonitrile. That could mean that the resonance-stabilizing effect (eq 7) probably has



(7)

a minor, but significant, contribution to the transition state. Thus only roughly Hammett relationships are observed; from the results of Table I β values of −3.10 and −2.37 are evaluated, respectively, with σ^+ (r = 0.94) and σ (r = 0.95) contstants.

Even if the polar effects govern the reactivity and selectivity, the overall effect is much less marked compared with dialkylamino radical cations; thus in the series benzonitrile, benzene, toluene, anisole, the relative rates of the para positions are respectively 0.025:1.00:4.23:20.10 with $\cdot^{+}NH_3$, whereas with $(CH_3)_2{}^{+}\dot{N}H$ the para position of toluene is 51 times more reactive than a position of benzene,[8] anisole is >10^3 times more reactive than benzene[9] and benzonitrile does not react. This last fact can be in part related to the competitive irreversible loss of a proton of the dimethylamino radical cation (eq 8). Evidence for

$$(CH_3)_2{}^{+}\dot{N}H \rightarrow CH_3NHCH_3\cdot + H^+ \rightleftarrows CH_3{}^{+}NH_2CH_2\cdot \quad (8)$$

this competitive process in homolytic aromatic amination by dialkylamino radicals has been recently[10] provided.

The two radicals $\cdot^{+}NH_3$ and $(CH_3)_2{}^{+}\dot{N}H$ are generated at the same temperature (~20 °C) but from different sources in different solvents; however, the difference of the polar effect is too high to be ascribed to these factors. The main reason for this behavior is, in our opinion, the influence of the enthalpy of the addition reaction on the polar effect. The energy of the bond $^{+}NH_3C<$ is larger than that of the corresponding $(CH_3)_2{}^{+}\dot{N}HC<$ bond so that a more exothermic process occurs for the addition to the aromatic ring of the radical $\cdot^{+}NH_3$ compared with $(CH_3)_2{}^{+}\dot{N}H$. This higher exothermicity is reflected in an earlier transition state with less charge-transfer character (eq 9). Both structures 1 and 2 contribute to determine the activation energy, but from the results of Table I it clearly appears that the contribution of 1 is more important. In the transition state leading to the aminocyclohexadienyl radical the contribution of the polar effect, as expressed by eq 9, is still more pronounced with dialkylamino radical cations. Thus $\cdot^{+}NH_3$ has a somewhat higher

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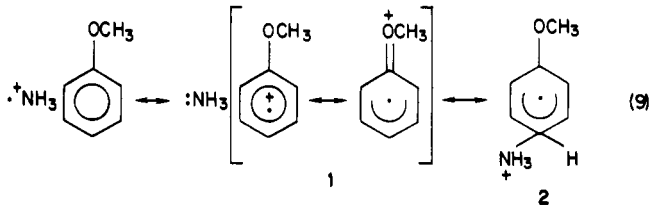
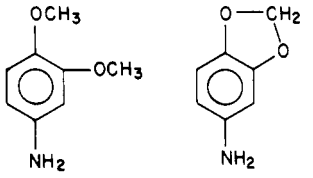


electron affinity than $(CH_3)_2{}^+\dot{N}H$, but it is a much less electrophilc species for enthalpic reasons. The same trend is observed in the reaction of oxygen-centered radicals: the electron affinity of ·OH, ·OR, and ·OOR radicals are quite close (respectively 1.83, 1.80, and 1.85 eV)[11] but the sensitivity to the polar effects increases as the reaction enthalpy decreases (·OH < ·OR < ·OOR).[12] The phenomenon is much more marked with protonated amino radicals than with oxygen-centered radicals because the enthalpy differences are higher with amino radicals with a positive charge on the nitrogen, which exalts the sensitivity to polar effects. All other conditions being equal, the lower the strength of the bond formed in the aromatic addition, the more the transition state would be similar to a charge-transfer complex and the more sensitive the reaction to polar effects. The absolute rate constants for the addition of the amino radical cations to the benzene ring are not known; the fact, however, that amino radical cations, intermediates in the Hofman–Löffler rearrangement, attack the benzene ring[13] indicates that the reaction is very fast since a value $>10^6$ s^{-1} has been estimated for the intramolecular hydrogen abstraction.[14] A still higher addition rate can be foreseen for the simple radical $\cdot{}^+NH_3$ for steric and enthalpic reasons.

From a synthetic point of view, the reaction has an undoubted interest for activated aromatic substrates under mild reaction conditions, particularly when the conventional methods present unfavorable selectivity problems. Thus an extensive investigation[15] has been carried out for the amination of 1,2-dimethoxybenzene and methylenedioxybenzene by HSA in order to obtain the commercially important amines **3** and **4**.

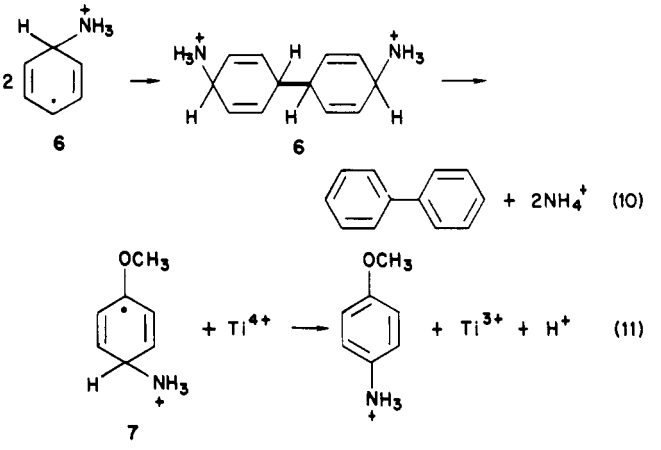


The conventional method of nitration and reduction shows disadvantages of positional selectivity, competitive oxidation, and hydrolysis. The amination by HSA very cleanly takes place under mild conditions with high positional and substrate selectivity; the best conditions involve the use of an acidic solution of dimethylformamide–water (1:1). The fact that the addition of the amino radical to the aromatic ring prevails over the hydrogen abstraction from dimethylformamide, present in large excess, further supports the very high rate of aromatic addition.

An intriguing aspect of the reaction concerns the ortho–para ratio in the amination of anisole. We have previously reported[3] that with the redox system $^+NH_3OH$/Ti(III) in methanol–aqueous solution the amination of anisole occurs, contrary to the behavior of benzene[2] which leads to the diaminodicyclohexadienyl **5**. These different results have been explained[2,3] by the fact that the low oxidizing power of Ti(IV) salt does not allow the oxidation of the aminocyclohexadienyl radical **6**, which dimerizes (eq 10). (The dimer **5** can lose NH_4^+, giving biphenyl),

Table III. Isomer Distribution in the Amination of Anisole by $^+NH_3OH$ and $^+NH_3OSO_3^-$

source of amino radical	metal salt	H_2SO_4 (mol per mol of anisole)	isomer distribution		
			o	*m*	*p*
$^+NH_3OSO_3^-$	Fe^{2+}		28.5	1.7	69.8
	Ti^{3+}		31.0	1.0	68.0
$^+NH_3OH$	Ti^{3+}		68.0	8.0	24.0
	Ti^{3+}	10	21.0	2.0	77.0



whereas the α-oxycyclohexadienyl radical **7** arising from anisole is more oxidizable and rearomatization occurs (eq 11). However, the ortho–para ratio in the amination of anisole was opposite for the two redox sources of the amino radical, $^+NH_3OH$/Ti(III) and HSA/Fe(II) under similar reaction conditions. This behavior has been now confirmed also in acetic acid–water solution (Table III).

Two different causes can be visualized to explain these results. (i) The rearomatization step can affect the positional selectivity. (ii) The reacting species are different with the two redox sources; three species can be envisaged: the unprotonated radical $\cdot NH_2$, the protonated radical $\cdot{}^+NH_3$, and the amino radical coordinated with the metal salt, $H_2\dot{N} \rightarrow M^{n+}$.

In order to have indications on the point ii the amination of anisole by $^+NH_3OH$/Ti(III) was carried out in the presence of a large excess of sulfuric acid. Actually under these conditions the ortho–para ratio of the anisole attack is reversed, approaching to the value obtained by HSA/Fe(II) (Table III). A possible explanation is that the redox system HSA/Fe(II) generates the protonated amino radical $\cdot{}^+NH_3$, whereas the source $^+NH_3OH$/Ti(III) produces a less selective Ti(IV) salt coordinated amino radical or the more selective protonated amino radical $\cdot{}^+NH_3$ depending on the acidity of the reaction medium.

Experimental Section

The reaction products were mostly commercially available compounds, in all cases known compounds easily available by conventional procedures. All the reaction products have therefore been identified by comparison (GC, IR, NMR, and MS) with authentic samples. Analytical GC employed a Carlo Erba 4200 or a Dani 3600 chromatograph, equipped with flame ionization detectors.

Competitive Kinetics. A flask, equipped with a magnetic stirrer, was charged with 2.1×10^{-2} mol of benzene and 2.1×10^{-2} mol of monosubstituted benzene (benzonitrile was used in com-

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petition with chlorobenzene), 2.1×10^{-3} mol of hydroxylamine-*O*-sulfonic acid and 0.017 g of $FeSO_4 \cdot 7H_2O$ in 24 mL of acetic acid and 12 mL of water. The solution was stirred at 40 °C for 2 h and then made basic with 30% NaOH and extracted with ether. GC analyses of the ethereal solutions were performed by using the following columns: OV 101 10% on Chromosorb W-HP-DMCS 80–100 mesh, capillary Carbowax (benzene, toluene, anisole, fluoro-, chloro-, and bromobenzene, *tert*-butylbenzene, benzonitrile); 3% Dexsil 300 on 100/120 Supelcopat (ethyl benzoate). Pure samples were used to check the response of the quantitative GC. The results are reported in Table I.

Synthetic Procedure. The procedure is substantially identical with that utilized in the competitive kinetics with the difference that only one aromatic substrate is used, and hydroxylamine-*O*-sulfonic acid is used in equimolecular amount with the aromatic substrate.

The reaction products were analyzed by quantitative GC, using the following internal standards: aniline (anisole, chlorobenzene, *tert*-butylbenzene, ethyl benzoate), *p*-xylene (benzene and toluene), *p*-chloroaniline (benzonitrile), chlorobenzene (fluorobenzene), *p*-methylaniline (bromobenzene). The results are reported in Table II.

Amination of 1,2-Dimethoxybenzene and (Methylenedioxy)benzene. A flask, equipped with a magnetic stirrer, was charged with 9.6 g of 1,2-dimethoxybenzene (or an equivalent amount of (methylendioxy)benzene), 8 g of hydroxylamine-*O*-sulfonic acid and 7 g of sulfuric acid in 50 mL of dimethylformamide and 50 mL of water; 1.9 g of $FeSO_4 \cdot 7H_2O$ was added and the resulting solution was stirred for 1 h at 30–35 °C. The solution was then made basic with 30% NaOH and extracted with ether. GC analysis of the ethereal extract (internal standard, aniline) revealed the presence of 3.6 g of 1.2-dimethoxybenzene, 6.3 g of 3,4-dimethoxyaniline, and 0.2 g of 2,3-dimethoxyaniline; conversion 62%. Yields of 3,4-dimethoxyaniline, based on converted 1,2-dimethoxybenzene, 96%.

With (methylendioxy)benzene the conversion is 45%; the yields of 4-amino(methylendioxy)benzene (93%) and 3-amino(methylenedioxy)benzene (4%) are based on the converted aromatic substrate.

Amination of Anisole by $^+NH_3OH$ and $^+NH_3OSO_3^-$ and $Ti_2(SO_4)_3$. A flask, equipped with a magnetic stirrer, was charged with 2×10^{-2} mol of anisole and 2×10^{-2} mol of hydroxylamine sulfate (or hydroxylamino-*O*-sulfonic acid) in 24 mL of acetic acid and 10 mL of water. A 20% $Ti_2(SO_4)_3$ solution was added under stirring at room temperature until the persistency of the violet color. The resulting solution was made basic, extracted with ether, and analyzed by GC. The results are reported in Table III.

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Registry No. $Ti_2(SO_4)_3$, 10343-61-0; $FeSO_4$, 7720-78-7; $\cdot^+NH_3$, 19496-55-0; $(CH_3)_2{}^+NH\cdot$, 34536-36-2; PhOMe, 100-66-3; PhMe, 108-88-3; Ph-*t*-Bu, 98-06-6; PhF, 462-06-6; PhCl, 108-90-7; PhBr, 108-86-1; PhCOOEt, 93-89-0; PhCN, 100-47-0; $^+NH_3OSO_3^-$, 2950-43-8; $^+NH_3OH$, 20712-83-8; 1,2-dimethoxybenzene, 91-16-7; (methylenedioxy)benzene, 274-09-9; 3,4-dimethoxyaniline, 6315-89-5; 4-amino(methylenedioxy)benzene, 14268-66-7.

Reaction of 1,2,3-Benzothiadiazoles with Radicophilic Alkenes and Alkynes in Di-*tert*-butyl Peroxide†

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The reaction of 6-X-1,2,3-benzothiadiazoles (**1**) with the radicophilic alkenes 1,1-diphenylethylene (**2**) and 1-cyano-1-(*tert*-butylthio)ethylene (**3**) and the alkynes PhC≡CR (**4**, R = H or Ph) in di-*tert*-butyl peroxide (TBP) leads to the cycloadducts **5**, **7**, and **8**. The proposed mechanism involves an initial attack by *tert*-butoxy radical at the sulfur atom of **1** affording the radical intermediate **9** which is responsible for the formation of all the reaction products.

Introduction

1,3-Dipolar cycloadditions of aromatic 1,2-ketocarbenes to unsaturated compounds are known to give fair to excellent yields of cycloadducts.[1] The analogous 1,2-thioketocarbenes, on the other hand, show a quite different behavior. The latter species, even though they afford high yields of cycloadducts in reaction with compounds containing carbon–sulfur double bonds, do not react at all or, at most, to a very small extent with alkenes, alkynes, nitriles, and aromatic compounds.[2] This behavior has been ascribed to the high reactivity toward radical species of the precursor of benzene 1,2-thioketocarbene, i.e., 1,2,3-benzothiadiazole. In fact, 1,2,3-benzothiadiazole is easily attacked by carbon, oxygen, and sulfur centered radicals, as well as by carbenes and nitrenes, giving a series of reactions of theoretical and, in a few cases, of synthetic interest.[3]

Results and Discussion

We report here that the addition of ring-substituted benzene 1,2-thioketocarbene equivalents to carbon–carbon multiple bonds can be achieved by an indirect method which allowed us to synthesize sulfurated cycloadducts not always easily accessible.

The reaction of 6-X-1,2,3-benzothiadiazole (**1**) with 1,1-diphenylethylene (**2**), 1-cyano-1-(*tert*-butylthio)-

† Dedicated to Prof. Giuseppe Leandri on his 70th birthday.

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