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Studies of tertiary amine oxides. 9. Thermal rearrangement of 1-(4-substituted-phenyl)piperidine N-oxide to the corresponding N-hydroxylamines

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(m, 6 H), 2.20–2.70 (m, 6 H), 5.80–6.00 (m, 1 H); IR (neat) 1705 (C=O), 1615 cm^{-1} (C=C); MS, m/z 152.1172 (calcd for $\text{C}_{10}\text{H}_{16}\text{O}$, 152.1201).

3-(2-Phenylethyl)-3-cyclopentenone (5f). An aqueous acetone (10 mL; water/acetone, 1/4) of ketal **16f** (200 mg, 0.87 mmol) and pyridinium *p*-toluenesulfonate (24 mg) was refluxed for 10 h. The cooled reaction mixture was poured into ice and water, and the product was extracted with pentane (50 mL \times 2). The pentane extract was washed with water (30 mL \times 3) and brine (30 mL), and dried over sodium sulfate. Filtration and solvent evaporation gave 133 mg (82%, 0.72 mmol) of an oil, which was

mostly 3-(2-phenylethyl)-3-cyclopentenone (**5f**). Isomer ratios of cyclopentenones were determined by GLPC (**5f**/**17f** = 85:15). **5f** was purified by column chromatography and preparative GLPC: ^1H NMR (CDCl_3) δ 2.20–3.10 (m, 8 H), 5.70 (m, 1 H), 7.20 (s, 5 H); IR (pentane) 1745 cm^{-1} (C=O); MS, m/z 186.1038 (calcd for $\text{C}_{13}\text{H}_{14}\text{O}$, 186.1044).

3-(2-Phenylethyl)-2-cyclopentenone (17f). This compound was isolated by column chromatography and preparative GLPC from the above reaction mixture: ^1H NMR (CDCl_3) δ 2.20–3.10 (m, 8 H), 5.93 (m, 1 H), 7.17 (s, 5 H); IR (pentane) 1710 cm^{-1} (C=O); MS, m/z 186.1123 (calcd for $\text{C}_{13}\text{H}_{14}\text{O}$, 186.1044).

Studies of Tertiary Amine Oxides. 9.¹ Thermal Rearrangement of 1-(4-Substituted-phenyl)piperidine *N*-Oxides to the Corresponding *N*-Hydroxylamines

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(4-Substituted-phenyl)piperidine *N*-oxides undergo a thermal rearrangement to *O*-arylhydroxylamines. Electron-withdrawing substituents are essential for the rearrangement and must be ortho or para relative to the >N–O function. The reaction has been found to be first order in substrate when rates were measured in dioxane, and the activation parameters were calculated. The order of reactivity in this rearrangement is $\text{NO}_2 \gg \text{CN} > \text{COPh} > \text{COMe} > \text{COOEt} > \text{CONH}_2$. The rates correlate very well with σ^- constants and the ρ value was positive and large (+3.6) pointing to a highly polar activated complex with an electron-rich reaction center. All results strongly support an intramolecular cyclic mechanism.

Pyrolysis of tertiary amine oxides involves three main reactions. Those *N*-oxides having a β -hydrogen atom undergo an elimination reaction often known as Cope elimination² with the formation of an olefin and a hydroxylamine. Those *N*-oxides that lack a β -hydrogen atom undergo on pyrolysis either an isomerization known as Meisenheimer rearrangement³ with migration of a group from N to O or a thermal deoxygenation to the corresponding tertiary amines.

The Meisenheimer isomerization is limited to certain groups. Benzyl⁴ and allyl⁵ groups were among the first recognized to undergo N to O shift. Groups observed later include neopentyl,⁶ homoadamantyl,⁷ and tetrachloropyridyl.⁸ The benzene nucleus, when substituted with an electron-withdrawing group, e.g., NO_2 , undergoes migration during pyrolysis of *N,N*-dimethylaniline *N*-oxides⁹ or (2- and 4-nitrophenyl)-piperidine *N*-oxides.¹⁰ This paper described the effect of five new substituents on the course of the rearrangement of *N*-arylpiperidine *N*-oxides.

Table I. Properties of the Amines 1

no.	yield, %	mp, C° (cryst solv)	λ_{max} , ^a nm (ϵ_{max})	^1H NMR, δ^b
1a ^c	100	103–104 (EtOH)	390 (21676), 232 (8250)	8.1 (d, 2 H, $J = 9.7$), 6.8 (d, 2 H, $J = 9.7$)
1b	96	52–54 (hexane)	298 (22870), 228 (8410)	7.4 (d, 2 H, $J = 9$), 6.8 (d, 2 H, $J = 9$)
1c	92	78–80 (petroleum ether)	322 (22320), 238 (8656)	7.4 (d, 2 H, $J = 9$); 6.8 (d, 2 H, $J = 9$)
1d	90	85–87 (EtOH– H ₂ O)	345 (19823), 247 (8212)	7.8 (d, 2 H, $J = 9$); 6.8 (d, 2 H, $J = 9$)
1e	90	73–75 (EtOH)	307 (22736), 227 (6990)	7.9 (d, 2 H, $J = 9$); 6.8 (d, 2 H, $J = 9$)
1f	85	192–194 (EtOH– H ₂ O)	295 (19690), 230 (6901)	7.9 (d, 2 H, $J = 9$); 6.9 (d, 2 H, $J = 9$)
1g	78	222–224 (benzene)	308 (24923), 230 (10250)	7.9 (d, 2 H, $J = 9$); 6.9 (d, 2 H, $J = 9$)

^a Solvent is dioxane. ^b J values are given in hertz. ^c Data of **1a** are taken from ref 10.

Results and Discussion

Synthesis. (4-Substituted-phenyl)piperidines **1**, were prepared by the reaction of 4-substituted-fluorobenzene with piperidine (Table I). *N*-Oxidation of the tertiary amines to the corresponding *N*-oxides **2** was accomplished with performic acid (Scheme I).

The crystalline tertiary *N*-oxides **2** were characterized by ^1H NMR, IR, UV, and elemental analysis. The physical and spectral properties of the *N*-oxides are listed in Table II.

In the ^1H NMR spectra, in general, all protons show a considerable downfield shift compared with the same protons in the corresponding tertiary amines. Such

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Table II. Properties of the Tertiary Amine Oxides 2 and Rearrangement Products 3^a

no.	yield, %	mp, C°	λ_{\max} , ^b nm (ϵ_{\max})	¹ H NMR, δ ^d
2a	67	150–153	254 (9162)	8.34 (s, 4 H)
2b	85	143–145	228 (16041)	8.2 (d, 2 H, $J = 9$), 7.8 (d, 2 H, $J = 9$)
2c	76	154–156	238 (15483)	8.22 (d, 2 H, $J = 9$), 8.1 (d, 2 H, $J = 9$)
2d	75	144–146	250 (14450)	8.2 (d, 2 H, $J = 9$), 7.9 (d, 2 H, $J = 9$)
2e	78	142–144	227 (11260)	8.1 (s, 4 H)
2f	80	201–203	229 (7680)	8.08 (s, 4 H)
2g	85	204–206	204 ^c (15370), 225 (10705)	
2h	87	167–169 (lit. ¹⁴ 169)	218 (6296)	8.1 (m, 2 H), 7.5 (m, 3 H)
3a	97		228 (6250), 308 (11476)	8.2 (d, 2 H, $J = 9.8$), 7.1 (d, 2 H, $J = 9.8$)
3b	95		220 (4762), 250 (17825)	7.5 (d, 2 H, $J = 9$), 7.1 (d, 2 H, $J = 9$)
3c	90		222 (7414), 270 (15150)	7.86 (d, 2 H, $J = 9$), 7.08 (d, 2 H, $J = 9$)
3d	92		225 (10662), 286 (12419)	7.84 (d, 2 H, $J = 9$), 7.18 (d, 2 H, $J = 9$)
3e	85		217 (7062), 257 (11890)	7.94 (d, 2 H, $J = 9$), 7.08 (d, 2 H, $J = 9$)
3f	82		232 (3033), 304 (7450)	7.74 (d, 2 H, $J = 9$), 7.08 (d, 2 H, $J = 9$)

^a Satisfactory analysis data were obtained for all new compounds. Data of 2a and 3a are taken from ref 10; mp for 2a is for the HCl derivative. ^b Solvent is dioxane. ^c Solvent is water. ^d J values are given in hertz.

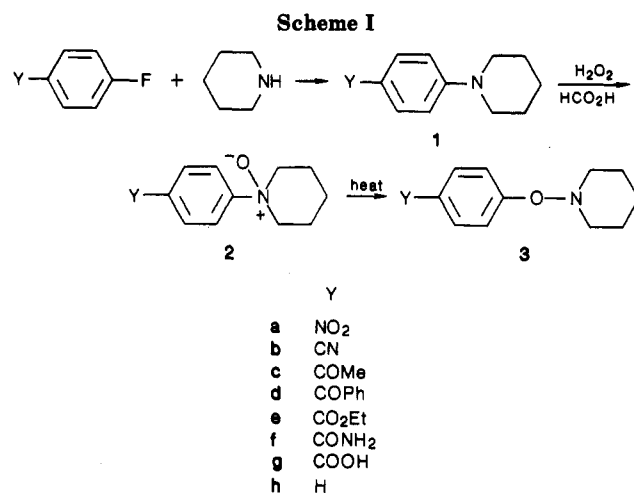
Table III. Kinetic Data for Thermal Rearrangement of the N-Oxides in Dioxane

no.	Y	σ	σ^-	$10^3 k_{70}$, min ⁻¹	E_a , kcal·mol ⁻¹	ΔS^\ddagger , eu	ΔG^\ddagger , kcal·mol ⁻¹	applicable temperature range, °C
2a ^a	NO ₂	0.81 ^b	1.27 ^b	70.90	20.27 ± 0.4	-15.1 ± 4.0	24.77 ± 1.6	55.0–80.0
2b	CN	0.70 ^b	1.00 ^b	4.56	22.33 ± 1.5	-14.5 ± 4.3	26.62 ± 3.0	65.0–90.5
2c	COMe	0.47 ^b	0.87 ^b	1.408	23.84 ± 1.8	-12.5 ± 5.9	27.43 ± 3.8	68.0–90.5
2d	COPh	0.459 ^c	0.88 ^c	1.571	23.87 ± 0.8	-12.2 ± 2.3	27.37 ± 1.6	70.4–90.1
2e	COOEt	0.44 ^b	0.68 ^b	0.383	25.02 ± 1.0	-11.6 ± 3.0	28.30 ± 2.4	71.4–92.8
2f	CONH ₂	0.36 ^c	0.63 ^c	0.32	25.67 ± 1.2	-10.1 ± 4.0	28.43 ± 2.6	72.0–92.4

^a Data are taken from ref 11. ^b Taken from ref 14a. ^c Taken from ref 14b.

downfield shift is due to the polar >N–O group, which affects the chemical shift of both heterocyclic and aromatic ring protons. In the spectrum of 2a,¹⁰ 2e, and 2f the aromatic protons appear as a single line in each case, apparently because these protons are under the deshielding influence of NO₂ or CONH₂ or CO₂Et and the >N–O group to approximately equal extent, thus representing what is called “deceptively simple AB spectra”.¹²

The amine oxides 2 undergo a thermal rearrangement to the O-arylhydroxylamines 3 in high yields when heated in dioxane (Table II, Scheme I). The structure of the rearrangement products was established by ¹H NMR, IR, and UV spectra and composition analysis. The spectral properties of the rearrangement products are listed in Table II. The kinetics of the rearrangement for each compound was studied in dioxane at four or five temperatures (temperature range 60–90 °C). The rate of this isomerization is clearly first order up to 3 half-lives. The rate was measured by using UV techniques. The mechanism of the rearrangement is best described as an intramolecular cyclic process, and such a mechanism is strongly supported by the results of the kinetics and of a cross-over experiment.¹⁰ The driving force for the rearrangement is related to the degree of electron deficiency at the aryl carbon atom directly attached to N. The more powerful the electron-withdrawing Y group, the more facile is the attack of the negatively charged oxygen of the >N–O function on the aryl carbon atom. It is not surprising, therefore, to notice that the rate of overall rearrangement is related to the degree of electron-withdrawal ability of the Y group.



It is worth noting that compound 2h is essentially unreactive in this rearrangement even at elevated temperature. This comes from the fact that an electron-withdrawing group must be present at the ortho and/or para position for the rearrangement to occur.^{9,10}

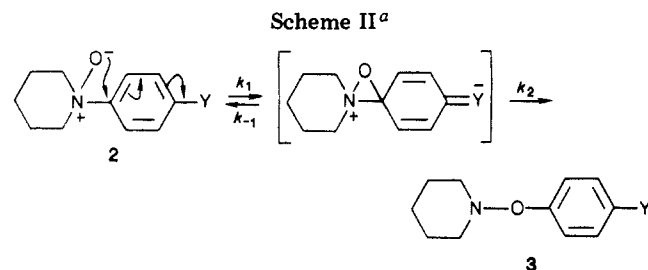
Activation Parameters. The activation parameters are listed in Table III. The free energies of activation are generally small in value and vary within 4 kcal/mol. Their values are proportional to the electron-withdrawing capability of the para substituents. The most powerful electron-withdrawing group NO₂ leads to the lowest free energy of activation (24.7 kcal/mol), while the least powerful electron-withdrawing group CONH₂ gives the highest value of ΔG^\ddagger (28.4 kcal/mol). This observation is explicable by the intramolecular nucleophilic attack of the oxygen atom of the N–O function on the aryl group (Scheme II).

The entropies of activation, ΔS^\ddagger , which are found in Table III are all largely negative (–10 to –15 eu) and this is in strong agreement with the involvement of a three-membered ring in the transition state which is required

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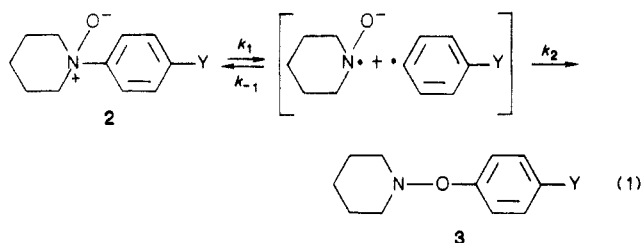
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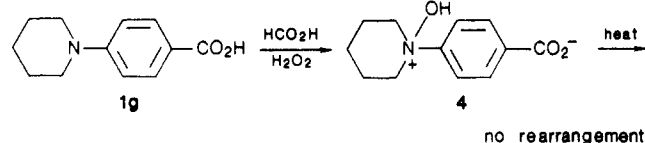


by the mechanism of Scheme II.

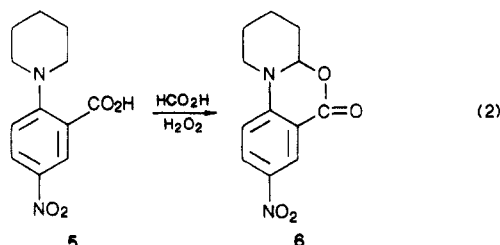
The negative values for ΔS^\ddagger exclude the possibility of the involvement of free radical particles as intermediates during the isomerization of the *N*-oxides 2 (eq 1).



Oxidation of (*p*-carboxyphenyl)piperidine (1g) gives anomalous results. The oxidation product 2g was isolated in fair yield as a colorless powder insoluble in most common organic solvents. Its properties and analytical data are consistent with an *N*-oxidized molecule but not with free (*p*-carboxyphenyl)piperidine *N*-oxide (2g). It is therefore suspected that 2g is in fact a zwitterion (4).



Compound 2g is stable to heat and does not undergo rearrangement on pyrolysis. The failure of the rearrangement process in 2g (4) is not surprising since the $>N-O$ group is protonated and its capability to attack the aryl carbon atom (Scheme II) is therefore largely reduced. In contrast Meth-Cohn and Suschitzky¹³ found that oxidation of (4-nitro-2-carboxyphenyl)piperidine (5) by performic acid produced the lactone (6) through Polonovski reaction (eq 2).



Structure-Activity Relationship. The influence of molecular structure on chemical reactivity has been studied for a wide variety of organic reactions by the application of Hammett and other related equations. The effect of the para substituents on the reactivity of the *N*-oxide molecules in this isomerization is found to be governed by the Hammett equation. Thus, a plot of $\log k$ vs. σ gave a fair correlation ($r = 0.890$) but a much better plot is obtained with $\log k$ vs. σ^- (Figure 1) with a correlation coefficient $r = 0.9839$. This is not unexpected since the reaction involves extensive delocalization and is initiated

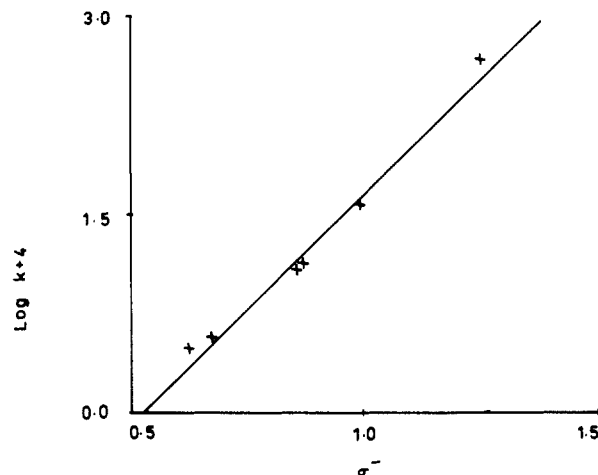


Figure 1. Plot of $\log k$ vs. σ^- for thermal rearrangement of tertiary amine oxides at 70 °C.

by a nucleophilic attack of the *N*-O moiety on the aromatic ring carbon. The large positive ρ value (+3.6) means that the reaction is strongly facilitated by reducing the electron density at the reaction center, i.e., the reaction rate is increased by the electron-withdrawing groups.

Experimental Section

Instrumentation. ¹H NMR spectra were recorded for identification purposes in deuteriochloroform solutions on a Bruker WH 90 spectrometer with tetramethylsilane as the internal marker. Ultraviolet spectra were recorded on a Pye-Unicam SP-1800 spectrophotometer. Melting points were determined with a Gallenkamp apparatus and were uncorrected. Elemental analysis was performed by Dr. Alfred Bernhardt, West Germany.

Syntheses. (1) **General Procedure for Preparation of the Tertiary Amines.** A mixture of 4-substituted-fluorobenzene (0.02 mol) and piperidine (0.06 mol) in dimethyl sulfoxide (50 mL) was stirred for 24–30 h at 70–80 °C. The tertiary amine was precipitated by the addition of water and recrystallized from the appropriate solvent, Table I.

(2) **General Procedure for Preparation of Tertiary Amine Oxides.** To an ice-cooled solution of the appropriate amine (0.02 mol) in 50–70 mL of 98% formic acid was added slowly 15 mL of 30% hydrogen peroxide. The reaction mixture was stirred for about 16 h at room temperature. The formic acid was neutralized with solid sodium carbonate, and the reaction mixture was extracted with three 150-mL portions of chloroform. Evaporation of chloroform produced the crude product, which was washed with dry ether and further purified by column chromatography with basic aluminum oxide. The *N*-oxide was released by elution with chloroform/methanol (3:1) and recrystallized from ethanol/ether or acetone/ether.

For oxidation of the amine 1g, the formic acid was evaporated in vacuo and the crude product was washed with acetone and recrystallized from water.

(3) **General Procedure for the Rearrangement of the *N*-Oxides.** Amine oxide 2a–f was heated at reflux in dry dioxane (70 mL) with constant stirring for 6 h. The solvent was stripped off and the product was chromatographed on neutral alumina with chloroform/petroleum ether as the eluent, giving the *N*-aryloxy amines 3a–f (Table II).

Kinetic Measurements. Reaction rates were determined spectrophotometrically by following the absorbance at λ_{\max} of the rearrangement product (3) as a function of time. Runs were carried out in duplicate at 75–85% completion. The specific temperature of the UV cuvette was maintained constant within ± 0.1 °C. A stock solution was obtained by dissolving 0.008–0.01 g of a freshly prepared oxide 2 in 10 mL of dry dioxane. A 0.2–0.4-mL sample was diluted with thermostated dry dioxane. Measurement of the absorbance began immediately. In all cases the "infinity" value A_∞ was determined experimentally for each run by leaving the solution of the amine oxide at the specified temperature until there was no further change in absorbance.

Reaction rate constants were calculated from the slope of $\ln(A_\infty - A_t)$ vs. time; the error in k_{obs} is $\leq 1-3\%$ for all the compounds examined. The energies of activation were calculated from the linear regression of $\ln k$ vs. $1/T$ by the least-square method and the entropies of activation were calculated by the standard formula derived from the absolute theory of reaction rates.

Registry No. 1a, 6574-15-8; 1b, 1204-85-9; 1c, 10342-85-5; 1d, 106947-61-9; 1e, 101038-65-7; 1f, 10552-10-0; 1g, 22090-24-0; 2a, 40832-54-0; 2b, 106947-62-0; 2c, 106947-63-1; 2d, 106947-64-2; 2e, 106947-65-3; 2f, 106947-66-4; 2g, 106947-67-5; 2h, 19555-50-1; 3a, 78039-75-5; 3b, 106947-68-6; 3c, 106947-69-7; 3d, 106947-70-0; 3e, 106947-71-1; 3f, 106947-72-2.

Binding of NH_4^+ to Azoles in the Gas Phase. A Theoretical Study of the $\text{N}\cdots\text{H}^+\cdots\text{N}$ Ionic Hydrogen Bond

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Ab initio calculations have been carried out for 20 B- NH_4^+ complexes, where B represents methylpyrazoles and methylimidazoles. The corresponding ionic hydrogen bonds are not linear. Deviations from linearity are small but reveal strong repulsive interactions between methyl substituents and the ammonium ion. In the equilibrium conformation of these complexes, the proton of the NH_4^+ system has been partially transferred to the azolic system. The distance between this proton and the basic center of the azole decreases as its proton affinity increases. The hydrogen-bond energies for these complexes increase with the proton affinity of the azole, but they are smaller than the corresponding proton affinities. This attenuation effect is slightly greater for pyrazoles than for imidazoles. Moreover, the dissociation energies of the corresponding ionic hydrogen bonds are linearly correlated to the 1s binding energy of the basic center of the azole. These linear relationships are different for α - and β -substituted compounds. Both pyrazoles and imidazoles behave as reasonably hard bases. Their absolute hardness decreases upon methyl substitution and varies like the ionization potential. The multivariate linear correlations, gas-phase basicities vs. 1s binding energies, and HOMO energies yield information on changes in hardness of the bases.

In the past two decades, great effort has been made in the field of gas-phase ion chemistry to investigate the intrinsic basicities and acidities of organic and inorganic species.¹ As a consequence, a large scale of gas-phase proton affinities is now available. In this context, one of the concepts that attracted attention was the existence of a regular alkyl-substituent effect. It seems now clear, for instance, that the presence of alkyl groups at the basic site of amines stabilizes the charge at the site. However, some results² questioned the systematic effect of alkyl substituents on the acidic or basic properties of some compounds. Moreover, the usual rules which establish, for instance, that substituting a hydrogen by an alkyl group increases the base strength, are not fulfilled when the reference acid is other than the proton³ (for instance, Li^+) because of specific characteristics of the acid-base interactions.

It seemed then interesting to study the behavior of known bases with regard to acids other than proton and to carry out a systematic analysis of possible substituent effects. To this respect, the theoretical calculations turned out to be a very useful tool and a quite convenient complement to the experimental work. In some cases, because the systems were not amenable to experiment or for other reasons, the only information regarding intrinsic basicities

of a given set of compounds came from SCF calculations. In the past few years we have devoted some effort to this kind of research. In a previous article⁴ we have discussed, by means of STO-3G SCF calculations, the systematic effect of methyl groups on the intrinsic basicity of pyrazoles and imidazoles, for which there was, at that time, an almost complete lack of experimental information regarding this particular effect.

In this paper, our aim is to analyze the same substituent effects when the reference acid is the ammonium ion. We consider it of interest to know the behavior of these azoles, whose chemistry is interesting per se, when they interact with an acid much softer than the proton. In particular, it seems appealing to know whether the substituent effects already investigated for the protonated species⁴ are still present when the reference acid is more complex. On the other hand, most of the attention regarding this particular problem has been directed to the study of alkali ion ($\text{Li}^{+3,5}$, K^{+6} , etc.) or other metal ion (C_pNi^{+5}) affinities, but very little has been done by using organic cations or ammonium ions. There are, however, some illustrative examples such as the work of Wood et al.⁷ on the methylation and ethylation of aniline, phenol, and thiophenol. Moreover, this study presents some additional interest because an analysis

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