I. ELECTROPHILIC REACTIONS OF p-TOLUENESULFONYL AZIDE

II. ^{15}N AND ^{13}C NUCLEAR MAGNETIC STUDIES OF ARYLDIAZONIUM COMPOUNDS EFFECT OF SUBSTITUENT, SOLVENT AND 18-CROWN-6

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Carla Jutta Casewit

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To Tante Renate

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ABSTRACT

PART I

ELECTROPHILIC REACTIONS OF p-TOLUENESULFONYL AZIDE

Section 1. Review of Electrophilic Reactions of p-Toluenesulfonyl Azide

The electrophilic reactions of p-toluenesulfonyl azide are reviewed using the principle of hard and soft acids and bases (HSAB).

Section 2. The Reaction of p-Toluenesulfonyl Azide with the Sodium Salt of p-Toluenesulfonamide

A number of concurrent reactions of p-toluenesulfonyl azide-3-^{15}N (I-3-^{15}N) with the sodium salt of p-toluenesulfonamide were followed by ^{15}N NMR. I-2-^{15}N is formed as a result of a degenerate diazo transfer by I-3-^{15}N to p-toluenesulfonamide anion. p-Toluenesulfonamide anion also reacts with I-3-^{15}N to give di-p-toluenesulfonamide and azide ion. The ^{15}N-labeled azide ion exchanges with I to give I-1-^{15}N. I also reacts with azide ion, yielding dinitrogen and p-toluenesulfinate anion. The sulfinate salt reacts readily and reversibly with I to give 1,3-di-p-toluenesulfontriazene anion, which provides another pathway for interconversion of I-3-^{15}N and I-1-^{15}N.

Section 3. The Reaction of p-Toluenesulfonyl Azide with Potassium Azide

The reaction of p-toluenesulfonyl azide with potassium azide-1-^{15}N has been examined in toluene and dichloromethane by ^{15}N NMR. In addition

to azide-ion exchange leading to I-1-^{15}N and I-3-^{15}N, the formation of I-2-^{15}N is indicated. Two mechanisms for this novel scrambling are proposed. Azide-ion metathesis involving reversible formation of an N-pentazole derivative from I and azide ion, followed by azide exchange could account for the formation of I-2-^{15}N. Alternatively, a scrambling route involving the reversible addition of p-toluenesulfonylnitrene to I-3-^{15}N can be envisioned. The inhibition of scrambling in dichloromethane by addition of iodide ion suggests that a discrete p-toluenesulfonyl azide - azide ion intermediate is involved in any case.

ABSTRACT

PART II

^{15}N and ^{13}C NUCLEAR MAGNETIC RESONANCE STUDIES OF ARYL-DIAZONIUM COMPOUNDS. EFFECT OF SUBSTITUENT, SOLVENT AND 18-CROWN-6.

^{15}N and ^{13}C shifts induced by addition of one equivalent of 18-crown-6 have been determined for several para-substituted aryldiazonium fluoborates in dimethylformamide. The α-nitrogen (N1) and para carbon (C4) shift upfield and the β-nitrogen (N2) and C1 shift downfield on complexation. The effect of solvent on the positions of the ^{15}N and ^{13}C resonances of p-(n-butyl)benzenediazonium fluoborate are small. The influence of substituents on the ^{15}N chemical shifts is relatively large and comparable to the effect of 18-crown-6. These ^{13}C and ^{15}N results, in conjunction with previous spectroscopic studies indicate that the crown ether complexed aryldiazonium cation is electronically more diazonium-like and less diazo-like than the uncomplexed form.

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PART II

^{15}N AND ^{13}C NUCLEAR MAGNETIC RESONANCE STUDIES OF ARYLDIAZONIUM COMPOUNDS. EFFECT OF SUBSTITUENT, SOLVENT AND 18-CROWN-6

PART I

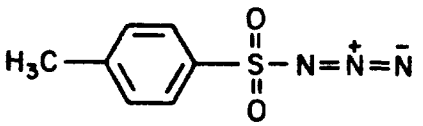
ELECTROPHILIC REACTIONS OF p-TOLUENESULFONYL AZIDE

SECTION 1

REVIEW OF ELECTROPHILIC REACTIONS OF p-TOLUENESULFONYL AZIDE.

INTRODUCTION

p-Toluenesulfonyl azide (I) is a highly versatile and useful reagent [1], which, depending on the conditions can act as an electrophile, nucleophile [2], 1,3 dipole [3] or source of p-toluenesulfonylnitrene [4].

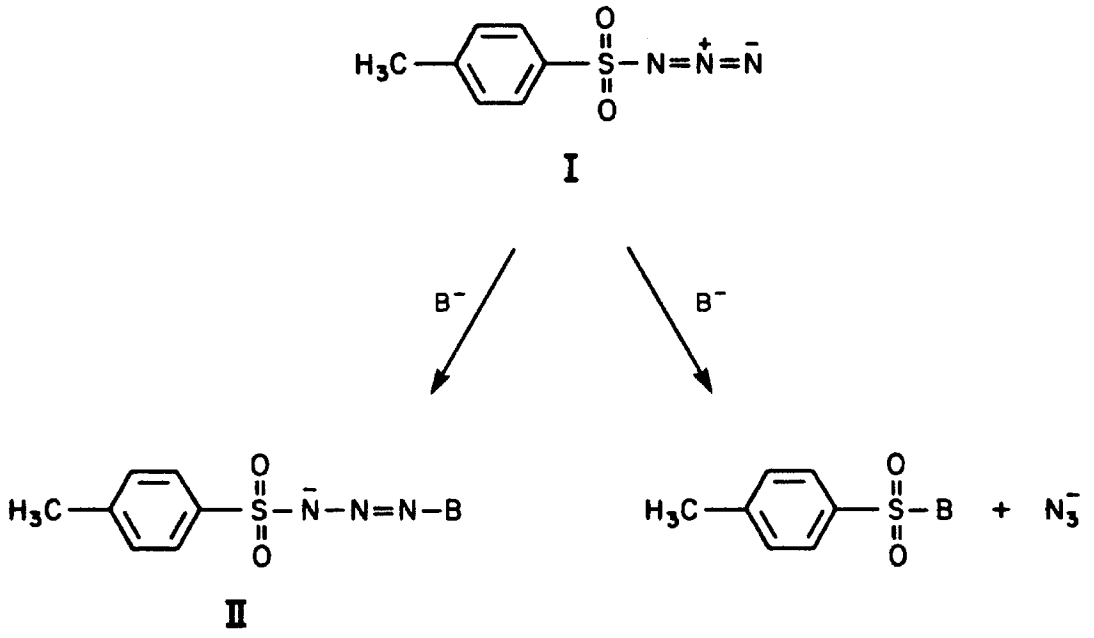


I

The chemistry of I with nucleophiles is particularly interesting because I is an ambident electrophile which can react both at the sulfur and at the terminal nitrogen. In the terminology of the theory of hard and soft acids and bases (HSAB) [5], the terminal nitrogen of I is a soft acid and the sulfonyl center is hard. This leads to a duality of reaction paths, where the nature of the nucleophile determines which site is preferentially attacked.

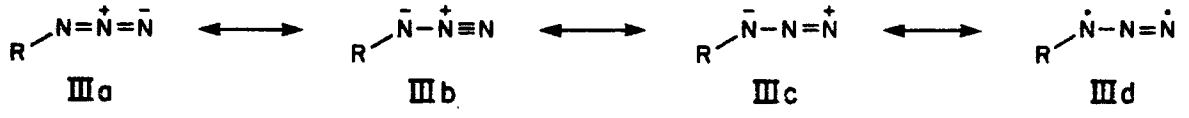
Soft nucleophiles tend to react at the terminal nitrogen of I to form a triazenyl anion (II) and hard nucleophiles at the sulfonyl to displace azide ion (scheme 1)

Scheme 1



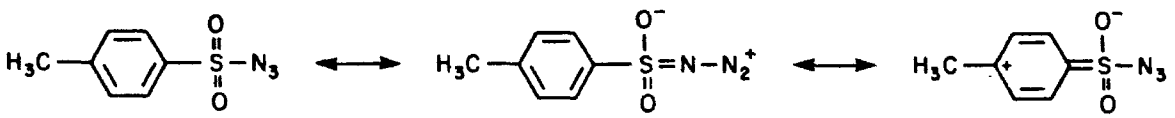
THE ELECTRONIC STRUCTURE OF I

No one resonance structure adequately accounts for the diverse chemistry of the azido group. Such groups are best described as resonance hybrids of several contributing structures, IIIa-IIId:



The N-diazonium resonance structures, IIIb and IIIc are useful in illustrating the electrophilic and nucleophilic character of the terminal and α-nitrogens, respectively. The relative contribution of a particular structure to the hybrid is expected to be greatly affected by the nature of R. Indeed, there are examples of azides with electron-withdrawing R groups which should be regarded as essentially the equivalent of N-diazonium compounds [6].

I should have at least some N-diazonium character because of the ability of the sulfonyl group to delocalize the negative charge on the α-nitrogen. One would expect that along with an increased contribution of resonance structure IVb, structure IVc would become less important.

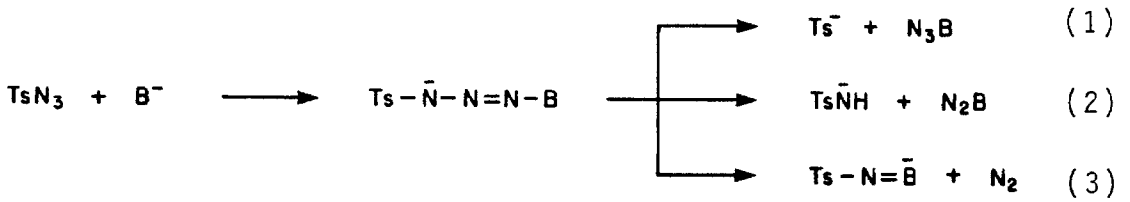


IVa IVb IVc

Evidence for the decreased importance of IVc is provided by the ^{13}C NMR of I and related compounds. The ^{13}C NMR of the carbon para to the SO_2N_3 group of I shows a 6 ppm upfield shift relative to the para carbon of p-toluenesulfonamide or p-toluenesulfonyl chloride [7]. Because para ^{13}C chemical shifts are dominated by mesomeric effects [8], the ^{13}C results indicate that the SO_2N_3 group increases the electron density of the para carbon relative to the SO_2NH_2 or SO_2Cl group.

NUCLEOPHILIC ATTACK AT THE TERMINAL NITROGEN OF I

The triazenyl anions formed by the nucleopholic attack of soft bases on the terminal nitrogen of I have been isolated in some cases. Triazenyl anions have been obtained from the reaction of I with 1-norbornyl anion [9], aryl grignard reagents [10], triphenyl phosphine [11] and several other bases [12]. These adducts may decompose either by the loss of p-toluenesulfinate (Eq. 1), loss of p-toluenesulfonamide anion (Eq. 2) or by extrusion of molecular nitrogen (Eq. 3).

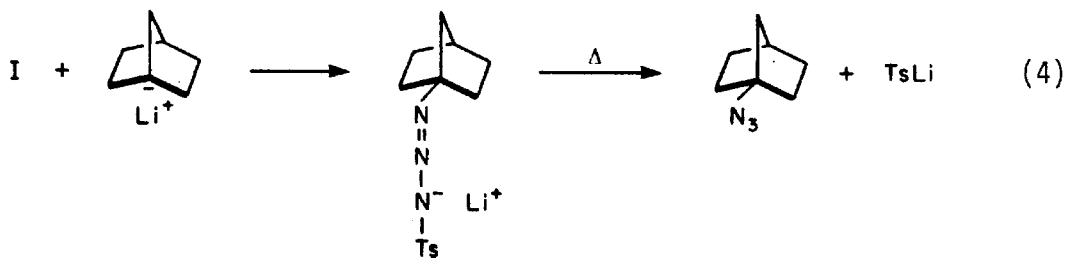


The nature of the base determines the decomposition route. Each pathway is discussed separately and in more detail below.

Azido-transfers

When the anionic nucleophile does not possess a labile α-hydrogen, decomposition of the triazenyl anion yields a new azide and the excellent leaving group p-toluenesulfinate anion. The azido-transfer

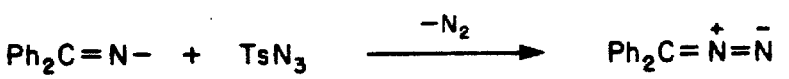
reaction is illustrated for the reaction of 1-norbornyl anion with I (Eq. 4).[9]



(4)

Use of I as an azido-transfer reagent is a relatively new development. In most synthetic procedures, the triazene salt is not isolated, but instead generated *in situ* to give the azide [13].

I has been found by Anselme and coworkers [14,15] to also transfer an azido group to nitrogen anions with no α-hydrogen (Eqs. 5-6).



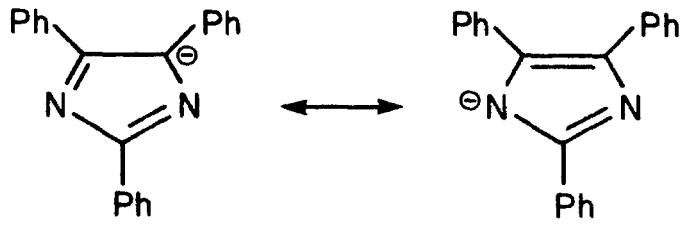
(5)

(6)

The detailed mechanism of these novel reactions is unknown. Anselme suggests that the initially formed triazenyl anion fragments to give an

N-azide. Subsequent loss of N_2 from the N-azide accounts for the observed products.

Azido transfer by I to an ambident nucleophile has been reported by Sakai and Anselme [16]. The products of azido transfer to 2,4,5-triphenylimidazole anion (V) can only be explained if C-azidation is favored over N-azidation almost 2:1:



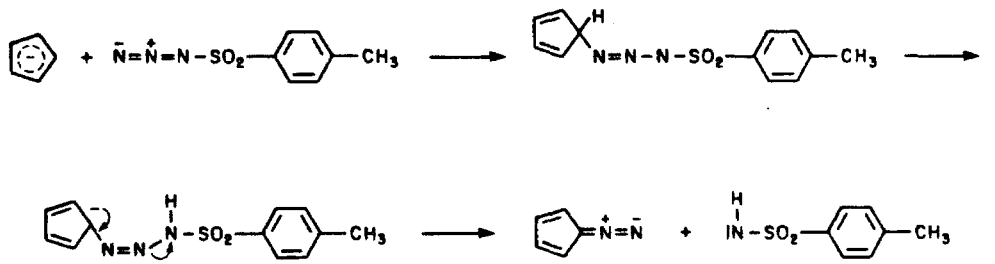
Va Vb

C-azidation was in fact unexpected, because such a reaction would disrupt the aromaticity of the heterocycle. However, this observation can be readily interpreted in terms of HSAB concepts. The products are a consequence of the preference for the soft terminal nitrogen of I to attack the softer carbon site rather than the harder nitrogen site of V.

Diazo-transfers

When I reacts with an anionic nucleophile possessing a labile α-hydrogen, azido transfer does not occur. Instead, the triazenyl anion is thought to tautomerize. The resulting triazene then decomposes into a diazo compound and the stabilized p-toluenesulfonamide anion. These

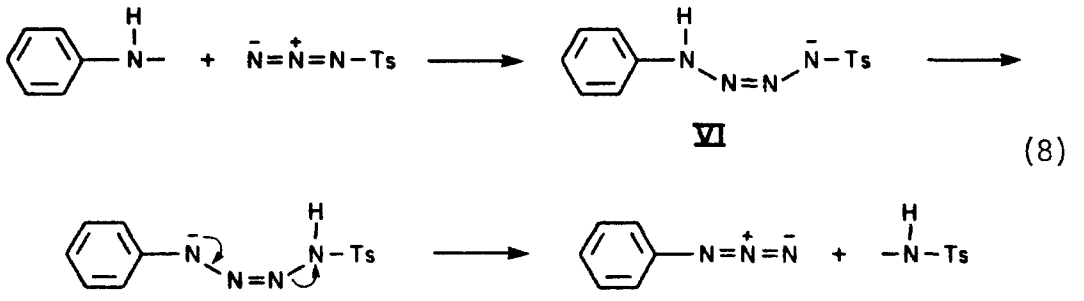
steps are illustrated for the reaction of I with cyclopentadienyl anion (Eq. 7).



(7)

Since the pivotal work by Doering and DePuy [17] in which I was employed to synthesize diazocyclopentadiene, I has been used to transfer diazo groups to a wide variety of active methylene groups in the presence of an organic base [18]. Indeed, use of I as a diazo-transfer reagent has stimulated the most synthetic interest, and considerable effort has been directed at improving isolated yields of diazo-transfers. Variations of the reagent and procedure include modification of the aryl nucleus of I [19,20b], phase-transfer catalysis [20] and immobilization of I on a polymer support [21].

Diazo group transfer has been extended to the anions of primary amines [19,22], hydrazines [23,24] and hydrazones [22]. The diazo transfer by I to amine anions has been developed into a useful synthesis of aliphatic and aromatic azides [19,22] (Eq. 8).

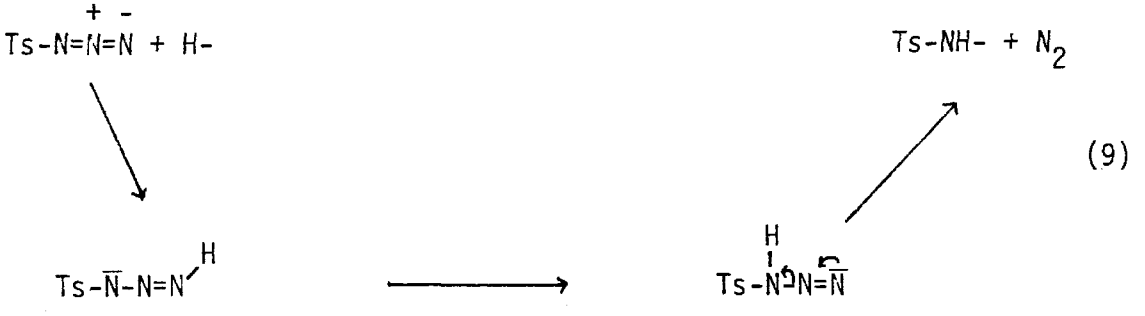


VI

(8)

Anselme and Fischer [22] have reported the isolation of an adduct from the reaction of the chloromagnesium salt of aniline with I, which decomposed on heating to give phenyl azide. This yellowish chloromagnesium salt is thought to be VI.

A novel reaction of I with sodium hydride (which acts as a soft base) has been reported by Lee and Closson [25]. This prototype diazo transfer yields p-toluene sulfonamide anion and molecular nitrogen: (Eq. 9)



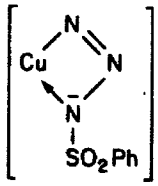
(9)

Loss of Molecular Nitrogen

I also forms triazene complexes with soft neutral bases. These triazenes decompose on heating to give a nitrene and molecular nitrogen. The Staudinger reaction is a classic example[11,26]. The phosphazide complex formed by reaction of I with triphenylphosphine loses molecular nitrogen to give a phosphine imine (Eq. 10):

$$Ts\text{-}\overset{+}{\overline{N}}\text{-}N{=}N\text{-}PR_3 \xrightarrow{\Delta} \left[Ts\text{-}N(\cdots N{=}N)\cdots PR_3 \right]^{\ddagger} \xrightarrow{-N_2} Ts\text{-}N{=}PR_3 \qquad (10)$$

A similar process is thought to occur in the activation of benzenesulfonyl azide by metallic copper. Kwart and Kahn [27] have investigated the copper-catalyzed decomposition of benzenesulfonyl azide and propose the formation of an arylsulfonyl azide-copper complex (VII):



VII

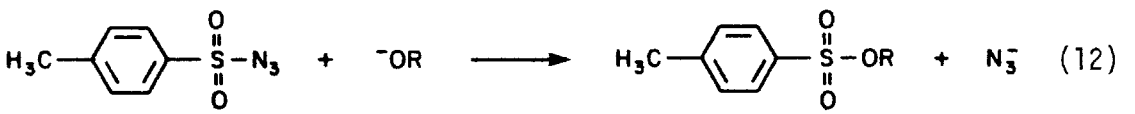
$$\left[\text{VII} \right] \longrightarrow \left[Cu{=}N\text{-}SO_2Ph \right] + N_2 \qquad (11)$$

There are many examples of activation of I by low-valent transition-metal complexes to give p-toluenesulfonylnitrene derivatives. The generated sulfonylnitrene is either trapped by co-ordinated ligands [28] on the metal or by added reagents [29]. These reactions may involve triazene-like intermediates, or more likely intermediates that bridge

the gap between Lewis acid-base complexes [30] and 1,3-dipolar addition complexes.

NUCLEOPHILIC ATTACK AT THE SULFONYL SULFUR OF I

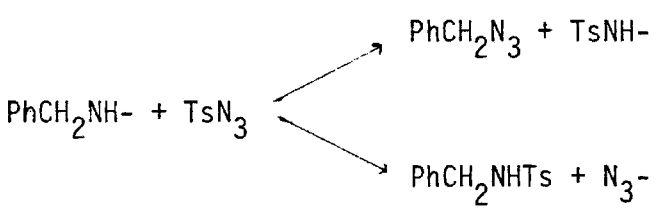
Nucleophilic attack occurs at the sulfonyl sulfur of I when the base is hard or borderline. Hard oxygen anions such as hydroxide, alkoxide, phenoxide and carboxylate [19] are known to displace azide ions from I (Eq. 12).



(12)

There have been no reports of the hard oxy bases attacking the soft terminal nitrogen of I.

The nitrogen bases studied by Anselme and coworkers [13-16,22,23] are somewhat softer than the oxygen bases discussed above and so nucleophilic attack occurs at both the terminal nitrogen and sulfonyl sulfur of I. For example, in the reaction of benzylamine anion with I: (Eq. 13)



(13)

both benzyl azide and N-benzyltosylamide were isolated [22]

The soft carbanions used in azido and diazo transfer procedures do not appear to attack the sulfonyl group.

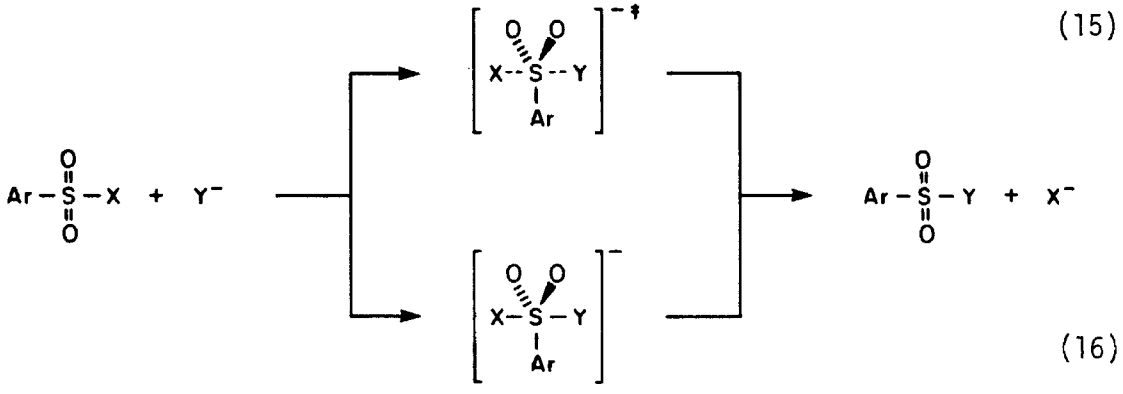
The Mechanism of Nucleophilic Substitution

The mechanism of the nucleophilic substitution at the sulfonyl center of I is unknown. However, other sulfonyl systems have been studied extensively, and the substitution mechanism is still a matter of considerable controversy. Depending on the system and solvent, dissociative, associative-concerted and associative-stepwise mechanisms have all been proposed.

The dissociative or S_N1 mechanism (Eq. 14) is thought to be followed in the hydrolysis of electron rich arylsulfonyl chlorides [31]:

$$ArSO_2X \longrightarrow ArSO_2^+ + X^- \xrightarrow{Y^-} ArSO_2Y \qquad (14)$$

Most substitutions at sulfonyl sulfur occur by an addition-elimination process, but there is disagreement on the details of the mechanism. The substitution may occur synchronously (Eq. 15) or in two steps through a discrete penta-coordinate intermediate (Eq. 16).



(15)

(16)

For most sulfonyl systems the existing evidence favors the concerted substitution (15) [32]. There are exceptions [33], however. Most recently, Engberts and coworkers [33a] provided evidence for an associative stepwise mechanism (Eq. 16) operating in the neighboring carbonyl-group catalyzed hydrolysis of arylsulfonamide derivatives. Unfortunately, a pentacoordinate sulfonyl addition intermediate has yet to be isolated by anyone.

Because of the marked dependence of the substitution mechanism on the system and conditions, no attempt will be made to predict the mechanism of azide ion displacement from I.

CONCLUSION

The concepts of the hard and soft acid and base theory can be

used successfully to understand and predict the reactions of I with nucleophiles. Whereas soft nucleophiles preferentially attack the terminal nitrogen, hard nucleophiles tend to attack the sulfonyl sulfur to displace azide ion. Borderline nucleophiles appear to react at both centers.

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SECTION 2

THE REACTION OF p-TOLUENESULFONYL AZIDE WITH THE SODIUM SALT OF p-TOLUENESULFONAMIDE

INTRODUCTION

To increase understanding of the reactions of p-toluenesulfonyl azide (I) with nucleophiles, the reaction of I with the sodium salt of p-toluenesulfonamide in dimethyl sulfoxide was examined.

The reaction of I (labeled with ^{15}N on the terminal nitrogen), and the sodium salt of p-toluenesulfonamide (generated *in situ* from excess p-toluenesulfonamide) was observed by ^{15}N NMR. Strong evidence was obtained by ^{15}N NMR for each of the reactions shown by Eqs. 1-3.

$$\text{Ts-N=N=}^{15}\text{N} + \text{Ts-}\bar{\text{N}}\text{H} \rightleftharpoons \text{Ts-N=}^{15}\text{N=N} + \text{Ts-}\bar{\text{N}}\text{H} \quad (1a)$$

$$\text{Ts-N=N=}^{15}\text{N} + \text{Ts-}\bar{\text{N}}\text{H} \rightarrow \text{Ts-NH-Ts} + \text{N=N=}^{15}\text{N}^{-} \quad (1b)$$

$$\text{Ts-N=N=}^{15}\text{N} + \text{N=N=}^{15}\text{N}^{-} \rightarrow \text{Ts}^{-} + 3\,^{15}\text{N}_2 \quad (2a)$$

$$\text{Ts-N=N=}^{15}\text{N} + \text{N=N=}^{15}\text{N}^{-} \rightleftharpoons \text{Ts-}^{15}\text{N=N=N} + \text{N=N=}^{15}\text{N}^{-} \quad (2b)$$

$$\text{Ts-N=N=}^{15}\text{N} + \text{Ts}^{-} \rightleftharpoons [\text{Ts-N}\cdots\text{N}\cdots{}^{15}\text{N-Ts}]^{-} \quad (3)$$

RESULTS AND DISCUSSION

Preparation of I-3-^{15}N

I-3-^{15}N was prepared by diazotization of p-toluenesulfonyl hydrazide with 30.2% enriched sodium nitrite, following the method of Curtius [1].

The report by Clusius and Weisser [2] that a similar preparation of phenyl azide-3-^{15}N resulted in the formation of 2-7% of phenyl azide-2-^{15}N made it necessary to determine if the labeling of I was completely specific. A ^{15}N spectrum of I-3-^{15}N in dimethyl sulfoxide indicated that within the limits of detection ($\sim$0.5%) only N3 was ^{15}N-labeled. It was found that I-3-^{15}N maintains its isotopic integrity in dimethyl sulfoxide for at least 34 h. However, on longer standing in dimethyl sulfoxide, isotope scrambling of I occurs. Approximately 20% I-1-^{15}N was observed by ^{15}N NMR after two weeks. Presumably a slow reversible ionization (perhaps solvent assisted) of I to p-toluenesulfonyl cation and azide ion takes place (4).

$$Ts\text{-}N{=}N{=}{}^{15}N \longrightarrow Ts^{+} + {}^{15}N_3^{-} \longrightarrow Ts\text{-}{}^{15}N{=}N{=}N \qquad (4)$$

Control experiments showed that unionized p-toluenesulfonamide does not react with I. The ^{15}N NMR spectrum of p-toluenesulfonamide and I-3-^{15}N in dimethyl sulfoxide showed that p-toluenesulfonamide does not scramble the ^{15}N label in p-toluenesulfonyl azide, even after 3 days.

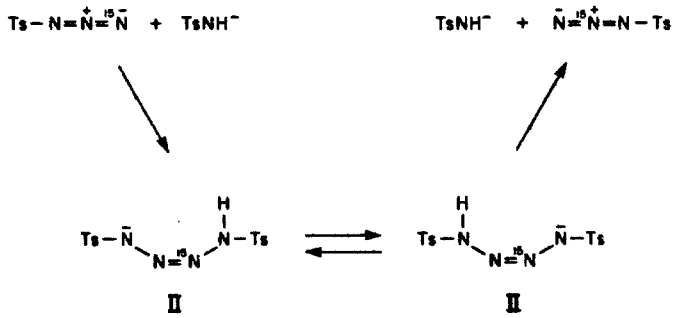
The Reaction of I-3-^{15}N with p-Toluenesulfonamide Anion

The ^{15}N spectra of I-3-^{15}N in the presence of the sodium salt of p-toluenesulfonamide, in dimethyl sulfoxide, show that within two hours I is completely scrambled and, in addition, many new ^{15}N-labeled

products are formed (Fig. 1). The ^{15}N signal assignments and chemical shifts are collected in Table I.

Formation of I-2-^{15}N

Work by Anselme and coworkers [3] on the diazo transfers by I to the magnesium salts of primary amines led us to expect that I would react with p-toluenesulfonamide anion in a similar manner. The diazo transfer by I to p-toluenesulfonamide ion is a degenerate reaction, and cannot be detected unless labeling techniques are employed. The diazo transfer by I-3-^{15}N to p-toluenesulfonamide anion, would be expected to result in the formation of I-2-^{15}N, through the intermediate tetrazenyl anion (II).



(5)

Fig. 1 clearly shows a signal due to I-2-^{15}N at 142.0 ppm. The I-3-^{15}N equilibrates with I-2-^{15}N within a few hours indicating that the degenerate diazo transfer is fast [4].

Related Reactions and Tetrazene Intermediates

The reaction of Eq. 5 is related to the reactions of aryldiazonium

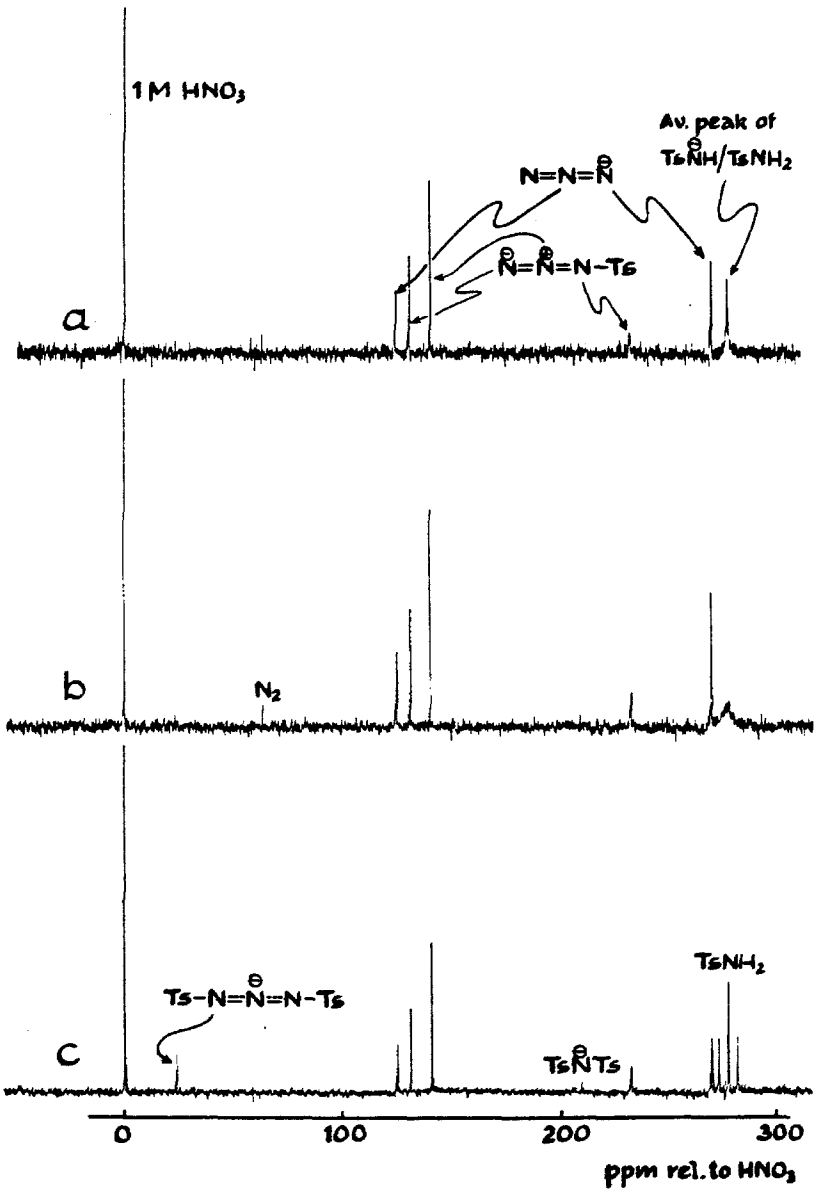


Figure 1. ^{15}N spectra of 5.0×10^{-3} mol sodium salt of p-toluenesulfonamide, 5.0×10^{-3} mol p-toluenesulfonamide and 8.1×10^{-3} mol p-toluenesulfonyl azide-3-^{15}N (I-3-^{15}N) in 20 ml of dry dimethyl sulfoxide; 20 μsec pulse angle, 10-sec repetition rate. Spectrum of sample (a) 10 min after preparation, 410 transients; (b) 5 h after preparation, 1015 transients; (c) 78 h after preparation, 1654 transients.

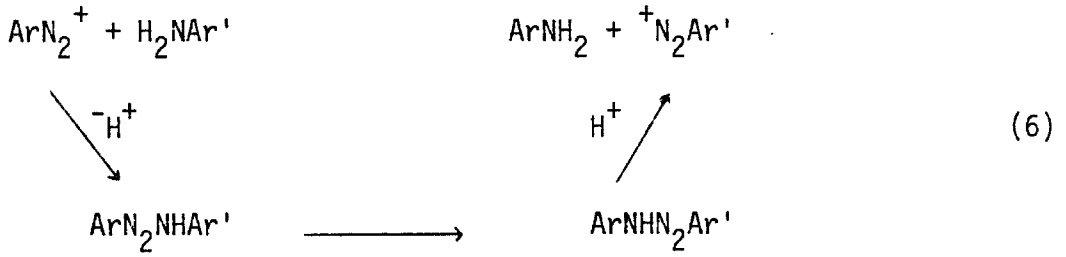
TABLE I. ^{15}N Signals in the Reaction of I-3-^{15}N with p-Toluenesulfonamide Anion

^{15}N Chemical Shift [a]	Assignment
24.1	N1 of 1,3-di(p-toluenesulfonyl) triazenyl anion
64.1	dinitrogen
125.8	N2 of azide ion
132.1	N3 of I
142.0	N2 of I
211.6	di-p-toluenesulfonamide anion
234.2	N1 of I
271.5	N1 of azide ion
279.0	p-toluenesulfonamide and its anion [b]

a) ppm relative to 1M external HNO_3

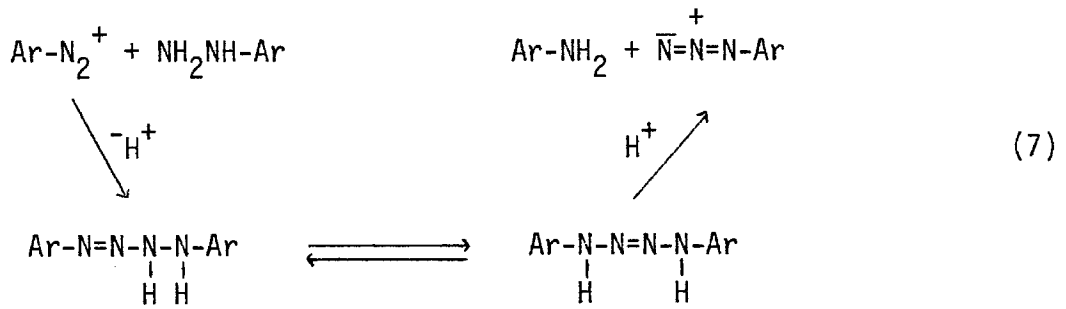
b) averaged because of fast proton exchange

salts with amines, but because diazonium salts are more nucleophilic than I, the amine need not be ionized in order to react [5]. The diazo migration [6] (Eq. 6)



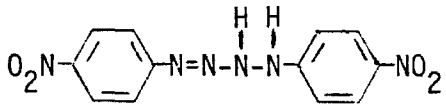
(6)

and the coupling of an aryldiazonium salt with an aryl hydrazine [7] (7) are examples of such reactions.



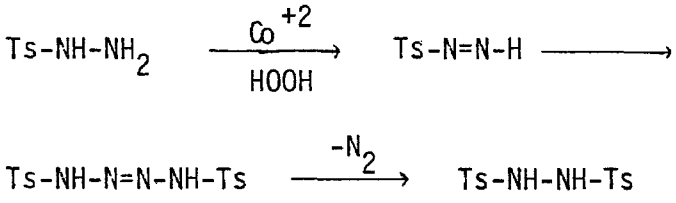
(7)

In contrast to the 1,4-di (p-toluenesulfonyl) tetrazenyl anion, II, 1,4-di(aryl)tetrazene intermediates appear to be relatively stable. Recently Evanochko and Shevlin [8] succeeded in isolating and characterizing 1,4-di(p-nitrophenyl)tetrazene (III) generated from the reaction of p-nitrophenylhydrazine with p-nitrobenzenediazonium tetrafluoroborate.



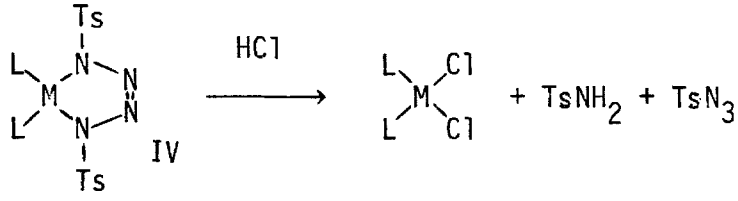
III

In a somewhat similar reaction, the oxidation of p-toluenesulfonylhydrazide is suggested to involve an intermediate 1,4-di(p-toluenesulfonyl)tetrazene [9] (8)



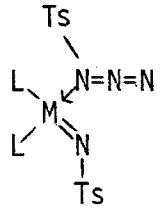
(8)

La Monica and coworkers [10] have isolated 1,4-bis(p-toluenesulfonyl)tetrazene complexes (IV) from the reaction of $Rh(NO)(PPh_3)_3$ with I. The tetrazene derivatives react with HCl to give p-toluenesulfonyl azide and p-toluenesulfonamide (9)



(9)

The authors suggest that IV is in equilibrium with an open form (V) which reacts with HCl. [10]



V

However, it is not necessary to invoke reaction of the open form to explain Equation 9, because this reaction follows naturally from Equation 5. Indeed, it is quite possible that the tetrazenyl anion (II) of Equation 5 is also an intermediate in Equation 9.

Interestingly, McDonald and coworkers [11a] have recently investigated the gas-phase reaction of phenylnitrene anion radical with phenyl azide by flowing afterglow. Anions are known to react at the nucleophilic γ-nitrogen of phenyl azide [11b] and nitrenes give products consistent with attack on the electrophilic α-nitrogen [11c]. Because the anion radical is ambiphilic, both sites of phenyl azide should be attacked. Indeed, products corresponding to addition at both the γ and α-nitrogen are observed (Eq. 10-11).

$$PhN^{\cdot -} + N_3Ph \rightarrow Ph\text{-}\bar{N}\text{-}N{=}N\text{-}\dot{N}\text{-}Ph \qquad (10)$$

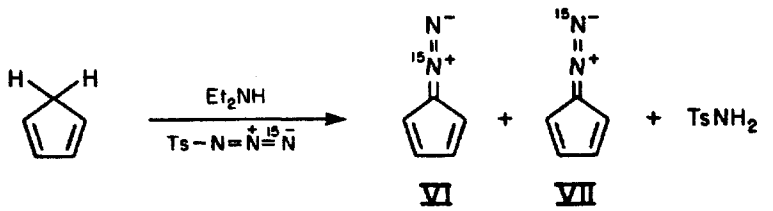
$$PhN^{\cdot -} + N_3Ph \rightarrow Ph\text{-}N{=}N\text{-}Ph^{\cdot -} \qquad (11)$$

Reaction 10 is quite analogous to the formation of III by the reaction of I with p-toluenesulfonamide anion.

Consequences of I-3-^{15}N Scrambling

The formation of I-2-^{15}N by the reaction of I-3-^{15}N with p-toluenesulfonamide anion may impose limitations on the utility of this reagent to specifically ^{15}N label diazo compounds.

Recently, I-3-^{15}N was used to synthesize labeled diazocyclopentadiene, and, contrary to expectations, the ^{15}N NMR spectrum of the product showed that, in addition to VI about 5% of VII was formed [12].



(12)

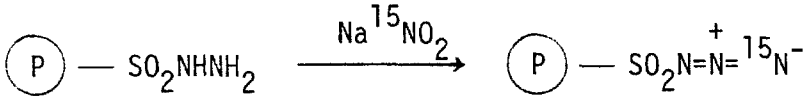
Because diethylamine catalyzes the ionization of cyclopentadiene (pK_a~15)[13] in the first step of the diazo transfer [14,15], it must certainly be able to convert p-toluenesulfonamide (pK_a 10.3)[16] to some extent to its conjugate base. The p-toluenesulfanamide anion so generated will scramble I-3-^{15}N by reaction 5. The reaction of the resulting I-2-^{15}N with cyclopentadienyl anion then accounts for the small amount of VII formed.

Although I-2-^{15}N is likely to be formed under the diazo-transfer conditions of Eq. 12, this may not be the only pathway leading to VII. The observation by Farnum and Yates [17] that α-diazoacetophenone transfers

a diazo group to the sodium salt of methyl phenylacetate suggests that a degenerate diazo transfer by diazocyclopentadiene to cyclopentdienyl anion could occur (13).

(13)

The bimolecular scrambling of I by p-toluenesulfonamide anion (Eq. 5) can be readily eliminated by employing a polymer support carrying sulfonylazido groups. This ^{15}N-labeled sulfonyl azide polymer could be prepared by diazotization of the poly(styrenesulfonylhydrazine) reported by Emerson and coworkers [18].



(14)

Using this sulfonyl azide polymer as a diazo-transfer reagent may provide a delicate probe for the importance of reaction 13.

Formation of di-p-Toluenesulfonamide

As discussed in Section 1, the hard and soft acids and bases (HSAB) principle [19] is very useful in understanding the reactions of I with nucleophiles. The borderline base p-toluenesulfonamide anion reacts with both the soft terminal nitrogen and the hard sulfonyl

sulfur of I.

$$TsN_3 + TsNH^- \longrightarrow TsNHTs + N_3^- \qquad (15)$$

Anselme[3] has noted a similar dichotomy in the reaction of magnesium salts of primary amines with I.

The azide ion generated in reaction 15 is visible in the ^{15}N spectra of Fig. 1 at 125.8 and 271.5 ppm [20]. Control experiments in dimethyl sulfoxide show that Eq. 15 is not appreciably reversible. It is suspected that strongly acidic [21] di-p-toluenesulfonamide protonates the azide ion and thereby inhibits the reverse reaction. In the reaction mixture of Fig. 1, however, the strongest base is p-toluenesulfonamide anion, and the following proton exchange occurs. The reaction of Eq. 16 has been verified by ^{15}N NMR.

$$TsNHTs + Ts\bar{N}H \longrightarrow Ts\bar{N}Ts + TsNH_2 \qquad (16)$$

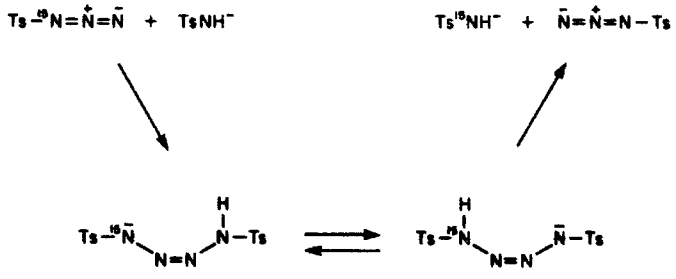
Eqs. 15 and 16 can account for the gradual transformation of the singlet at 279 ppm (Fig. 1a) to the triplet at 279 ppm [22] (Fig. 1c). The singlet in Fig. 1a arises from p-toluenesulfonamide in equilibrium with a small amount of p-toluenesulfonamide anion (only one peak is observed because of fast proton exchange). In Fig. 1c (78 h after sample preparation) all of the anion is consumed and only p-toluenesulfonamide remains so that a triplet results. The resonance of the anion of the strongest acid, di-p-toluenesulfonamide, is now visible

at 211.6 ppm, and this anion is not basic enough to exchange rapidly with p-toluenesulfonamide.

Formation of ^{15}N-labeled p-Toluenesulfonamide

The resonances of p-toluenesulfonamide and its anion in Fig. 1 are observed only because these materials have become enriched with ^{15}N. No ^{15}N signal was observed with a natural-abundance sample of p-toluenesulfonamide in dimethyl sulfoxide at a concentration and with an acquisition time comparable to the spectrum in Fig. 1c.

Formation of ^{15}N-labeled p-toluenesulfonamide and its anion is not consistent with the equilibrium of Eq. 5, although the same sequence of reactions with I-1-^{15}N would lead to labeled p-toluenesulfonamide (Eq. 17).



(17)

The two pathways leading to the formation of I-1-^{15}N will be discussed in the following paragraphs.

Exchange of Azide Ion

The first route for I-1-^{15}N formation is associated with the direct nucleophilic attack of azide ion on I. A ^{15}N spectrum of sodium azide and I-3-^{15}N in dimethyl sulfoxide showed signals at 132.1

ppm (I-3-^{15}N), 234.6 ppm (I-1-^{15}N) and 271.5 ppm (sodium azide-1-^{15}N), indicating fast azide exchange (Eq. 18).

$$Ts\text{-}N{=}\overset{+}{N}{=}{}^{15}N^{-} + N{=}N{=}N^{-} \longrightarrow Ts\text{-}N{=}\overset{+}{N}{=}\overline{N} + N{=}N{=}{}^{15}N^{-} \longrightarrow Ts\text{-}{}^{15}N{=}\overset{+}{N}{=}\overline{N} + N{=}N{=}N^{-} \qquad (18)$$

The reaction of Eq. 18 must occur by an addition-elimination mechanism rather than by dissociation-recombination because the 1,3-scrambling is greatly accelerated by azide ion.

Azido Transfer to Azide Ion

In Fig. 1 two small resonances appear at 64.1 and 24.1 ppm. These signals are also observed in solutions of I-3-^{15}N and sodium azide in dimethyl sulfoxide. The resonance at 64.1 ppm is attributed to ^{15}N-labeled dinitrogen. This assignment is based on the reported ^{15}N shift of dinitrogen of 66.5±1 ppm in benzene [23]. In addition, this 64.1 ppm signal disappears on purging solutions of p-toluenesulfonamide anion and I-3-^{15}N with dry unlabeled nitrogen and then slowly re-appears over several hours.

We propose that dinitrogen is evolved in a novel reaction in which I formally transfers an azido group to azide ion [24,25] (Eq. 19)

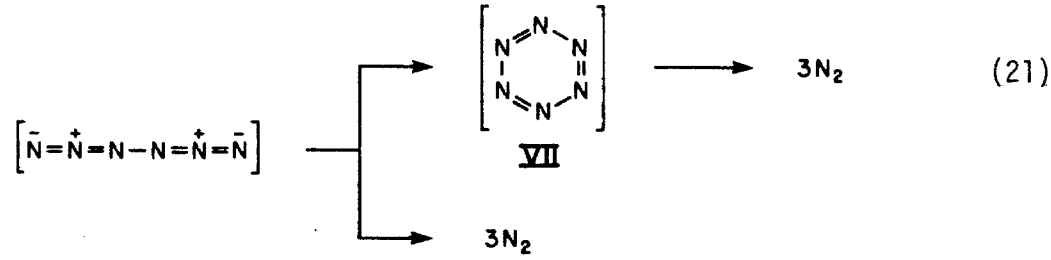
$$TsN_3 + N_3^- \longrightarrow Ts^- + 3N_2 \qquad (19)$$

Though reaction 19 was unexpected, HSAB theory predicts that the borderline base, azide ion, should react both at the sulfonyl sulfur and the terminal nitrogen of I.

Several mechanisms for this slow transformation may be envisioned. The simplest involves a straightforward nucleophilic coupling of I and azide ion to give the unknown free pseudohalogen $(N_3)_2$ [26] (Eq. 20).

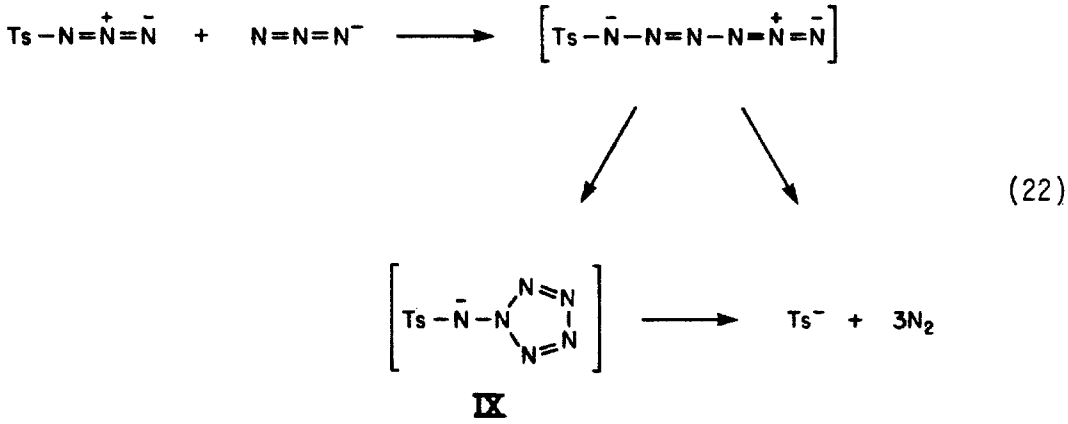
$$Ts\text{-}N{=}N{=}N + N{=}N{=}N^{-} \longrightarrow Ts^{-} + [N{=}N{=}N\text{-}N{=}N{=}N] \qquad (20)$$

The azide dimer [27] could decompose directly to $3N_2$ or else cyclize to hexazine [28] (VIII), before decomposing (21).



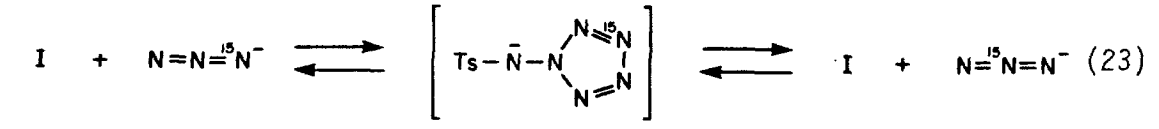
(21)

Alternatively, intermediates similar to those proposed in the coupling of azide ion with aryldiazonium salts could be involved [29].



(22)

Distinction between the mechanisms of Eqs. 21 and 22 by ^{15}N labeling is possible if the formation of IX were reversible (Eq. 23).



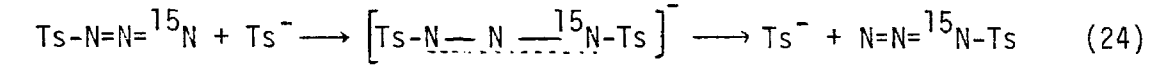
(23)

However, the ^{15}N spectrum of potassium azide-1-^{15}N and I in dimethyl sulfoxide after 8 h showed no scrambling of the potassium azide. This result therefore excludes pentazole reversibility but not irreversible formation of IX.

The reaction of I with azide ion in other solvents was investigated in order to probe the mechanism of this unique reaction. The results of this study are reported in Section 3 of this thesis.

Formation of 1,2-di(p-Toluenesulfonyl) Triazenyl Anion

The second route which interconverts I-3-^{15}N to I-1-^{15}N involves p-toluenesulfinate anion, formed in the reaction of Eq. 19 by way of a degenerate azido transfer with I through the intermediate triazenyl anion X (Eq. 24).

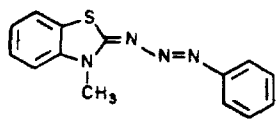


(24)

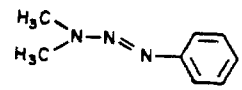
The ^{15}N NMR of I-3-^{15}N in the presence of small concentrations of the sodium salt of p-toluenesulfinic acid (dihydrate) in dimethyl sulfoxide

shows that the reversible complexation of the soft terminal nitrogen of I by the soft sulfur of the sulfinate anion occurs readily. Both I-3-^{15}N and I-1-^{15}N are visible in about equimolar amounts within 4 h. Thus, reaction 24 as well as reaction 18 allow for the formation of I-1-^{15}N from I-3-^{15}N.

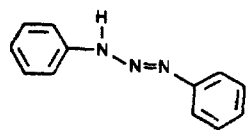
If an excess of the sulfinate salt is added to I-3-^{15}N in dimethyl sulfoxide, a concentration builds up of the triazene salt. The ^{15}N NMR of multilabeled I with an excess of the sulfinate salt (as the dihydrate) in dimethyl sulfoxide shows that no I remains, and only ^{15}N signals attributed to N1 (24.2 ppm) and N2 (-160.3 ppm) of X are observed. ^{15}N chemical shifts have been reported for triazenes XI [30a], XII [30b], and XIII [30c-d] (Table II).



XI



XII



XIII

The nitrogens of triazenyl anion are substantially deshielded relative

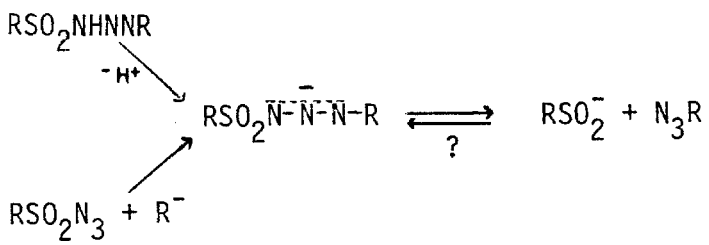
to the triazenes listed in Table II. The paramagnetic shift of X is probably primarily a consequence of increased N-lone pair delocalization [31] because of ionization.

The ^{15}N spectrum of a concentrated solution of multilabeled I and sodium azide in dimethyl sulfoxide after the gas evolution has stopped is shown in Figure 2. The resonances of X are visible, the azide ion becomes ^{15}N-labeled in accord with Eq. 18, and, in agreement with Eq. 19, the resonances of a small amount of labeled dinitrogen is observed.

Triazenyl Anions and Reaction of Azides with Sulfinate Salts

The formation of *diaryl* [32a], *dialkyl* [33] *and sulfonyltriazenyl* [32b] anions by deprotonation of the parent triazene is well documented. In addition, triazenyl anions can be formed by the reaction of a carbanion with an alkyl [11b], aryl [11b] or sulfonyl azide [34]. As noted in Section 1, sulfonyltriazene salts decompose readily into the sulfinate salt and azide (Scheme 1).[34]

Scheme 1



The reverse reaction, addition of sulfinate salts to organic azides,

TABLE II. ^{15}N NMR Chemical Shifts of Triazenes [a]

Compound	δN1	δN2	δN3	reference
XI	+78.2	-118.3	-56.4	30a
XII	+220.8	- 76.0	+16.0	30b
XIII	+200	-	+ 9	30c
XIII [b]	+ 96.5	- 65.6	+96.5	30d
X	+ 24.2	-160.3	+24.2	-

a) ppm relative to HNO_3

b) N1 and N3 are averaged because of fast proton exchange

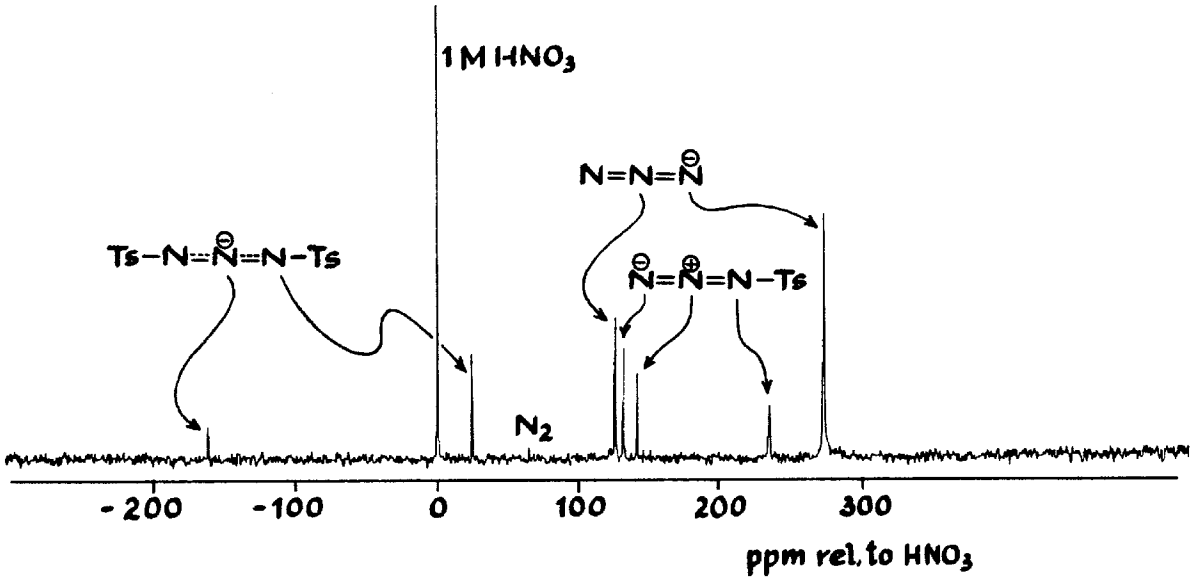


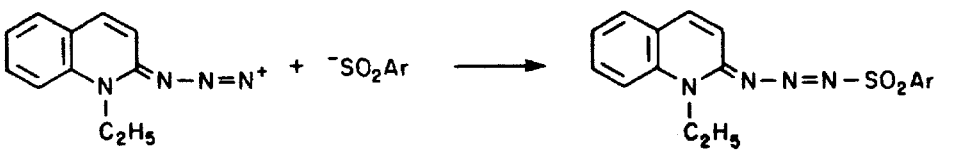
Figure 2. ^{15}N spectrum of 1.2×10^{-2} mol scrambled p-toluenesulfonyl azide (1-^{15}N, 2-^{15}N, 3-^{15}N) and 1.2×10^{-3} mol sodium azide in 25 ml dry dimethyl sulfoxide. The spectrum was taken 53h after sample preparation using 200 μsec pulse angle, 10-sec repetition rate, 1949 transients.

has not been systematically investigated. It should, however, be quite general. The first reported example appears to be the reaction of carbamoyl azides with arylsulfinate salts [35a] (Eq. 25).

$$ArSO_2Na + N_3\overset{O}{\overset{\|}{C}}NHR \xrightarrow[2)\ HCl]{1)\ \Delta} ArSO_2NH\overset{O}{\overset{\|}{C}}NHR \qquad (25)$$

Whether the sulfonylureas are derived from the decomposition of a sulfonyltriazenyl intermediate or from the reaction of a nitrene is not known.

The azidinium salts studied by Balli [25] have also been found to form complexes with sulfinate salts:



(26)

Considering the reaction of azidinium salts with arylsulfinate salts (Eq. 26), it is not surprising to find a counterpart to reaction 24 in aryldiazonium chemistry [35b] (27).

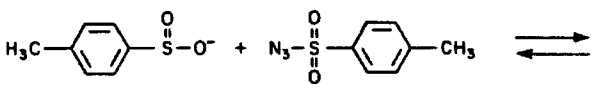
$$ArN_2^+ + HO\overset{O}{\overset{\|}{S}}Ar \xrightarrow{-H^+} Ar\text{-}N{=}N\text{-}\overset{O}{\overset{\|}{\underset{O}{S}}}\text{-}Ar \qquad (27)$$

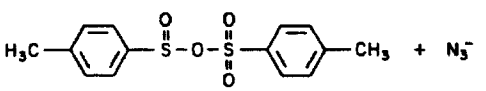
Formation and Reaction of p-Toluenesulfonyl Sulfinyl Anhydride

An ^{15}N spectrum of a mixture of multilabelled I in dimethyl sulfoxide treated with an equimolar amount of the sodium salt of p-

toluenesulfinate (dihydrate) shows two signals at 128 and 250 ppm after one week. A resonance at about 250 ppm is also visible in the ^{15}N spectrum of a solution of I-3-^{15}N treated in the same manner. The signals at 128 and 250 ppm are attributed to ^{15}N label at the N2 and N1 of a mixture of hydrazoic acid and azide ion [36].

The source of the azide ion is very likely the slow reaction of the sodium salt of p-toluenesulfinate at the sulfonyl sulfur of I. In this case, because the sulfonyl of I is a hard acid, the harder oxygen of the ambident anion is the attacking center [37] (Eq. 28).



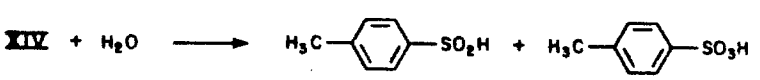


XIV

(28)

A precedent for reaction 28 is found in the studies by Corson and Pews [38] of the reaction of the sodium salt of p-toluenesulfinate with p-toluenesulfonyl chloride. The initial product, which was not isolated but instead reacted further under their reaction conditions, was thought to be the sulfonyl sulfinyl anhydride (XIV).

Under our experimental conditions, the sulfonyl sulfinyl anhydride would be expected to be hydrolyzed readily by the ambient water in solution (Eq. 29).



(29)

The p-toluenesulfinic and sulfonic acids should protonate the azide ion generated in reaction 28 to some extent, in agreement with the observed ^{15}N shifts.

Reaction 28 is far slower than formation of the triazenyl anion (X). However, because formation of X is reversible and reaction 28 is not (under hydrolysis conditions), formation of hydrazoic acid and azide ion should result. When the sulfinate salt is generated in situ, as in reaction of I with azide ion, the equilibrium of reaction 28 should lie far to the left because of the large excess of azide ion. In addition, the absence of water in solution precludes reaction 26 from driving reaction 28 to the right. As expected, Fig. 2 shows no evidence for the formation of hydrazoic acid.

Cleavage of 1,3-di(p-Toluenesulfonyl) Triazenyl Anion in Acid

Both diaryl and 1-arylsulfonyl-3-aryltriazene are cleaved by acids to an aryldiazonium salt and an amine [32] (Eqs. 30-31).

$$ArNHN_2Ar \xrightarrow{H^+} ArNH_2\overset{+}{N}_2Ar \longrightarrow ArNH_2 + {}^{+}N_2Ar \qquad (30)$$

$$ArSO_2NHN_2Ar \xrightarrow{H^+} ArSO_2NH_2\overset{+}{N}_2Ar \longrightarrow ArSO_2NH_2 + {}^{+}N_2Ar \qquad (31)$$

These acid-induced decompositions are the reverse of the coupling procedures for making the triazenes.

The ^{15}N NMR of a solution of X (generated in situ by addition of

the sodium salt of p-toluenesulfinic acid to I-3-^{15}N in dimethyl sulfoxide), acidified with trifluoroacetic acid or acetic acid, shows that X decomposes into I-3-^{15}N,I-1-^{15}N and presumably sulfinic acid (Eq. 32).

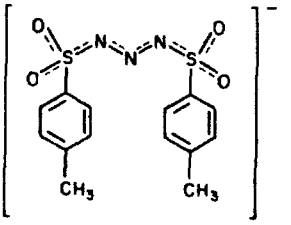
$$[ArSO_2\dot{N}\text{-}\dot{N}\text{-}\dot{N}SO_2Ar]^- \xrightarrow{H^+} ArSO_2H + N_3SO_2Ar \qquad (32)$$

There is no evidence for the intermediate formation of 1,3-di(p-toluenesulfonyl)triazene (XV):

$$ArSO_2\text{-}NH\text{-}N{=}N\text{-}SO_2Ar$$

XV

Instead, it appears that the highly delocalized anion (X) is preferentially protonated at the hard oxygen site of the sulfonyl. This oxygen-protonated tautomer of XV then decomposes into I and p-toluenesulfinic acid.



X

This mode of decomposition is consistent with the principles of HSAB.

CONCLUSION

The reactions of I-3-^{15}N with several nucleophiles in dimethyl sulfoxide studied here by ^{15}N NMR enlarge the scope of p-toluenesulfonyl azide reactivity. The principles of HSAB are very useful in rationalizing the course of these reactions. Soft nucleophiles, such as the sulfur of p-toluenesulfinate, preferentially attack the terminal nitrogen of I, giving adducts similar to those arising from the reaction of aryldiazonium salts with those nucleophiles. Hard nucleophiles, such as the oxygen of p-toluenesulfinate, appear only to react with the sulfonyl of I to displace azide ion. Borderline nucleophiles, such as azide ion or p-toluenesulfonamide anion, show both types of reactivity.

These investigations also impose limitations on the utility of this reagent. The 2,3-nitrogen scrambling of I by p-toluenesulfonamide anion indicates that completely specific ^{15}N labeling of diazo compounds with I-3-^{15}N may be difficult, if not impossible. Indeed, if I-3-^{15}N had been employed to synthesize diazocyclopentadiene by the classic route of Doering and DePuy [39], using the lithium salt of cyclopentadiene, completely ^{15}N-scrambled diazocyclopentadiene would surely have resulted. Furthermore, the sequestering of p-toluenesulfonyl azide by p-toluenesulfinate anion requires that the yields in azido-transfer reactions using I must be poor, as has been observed.

EXPERIMENTAL

The ^{15}N NMR spectra were taken at 18.25 MHz with a Bruker WH-180 spectrometer, using 15-25 ml samples in 25-mm sample tubes. A 5-mm concentric tube containing a solution prepared by dissolving sufficient $H^{15}NO_3$ in D_2O to give a 1-M acid concentration provided lock and reference signals. Chemical shifts are reported in ppm upfield from external HNO_3. All spectra were proton-coupled, and observations were made at ambient probe temperature, which was approximately 22°C.

Unless otherwise specified, dimethyl sulfoxide was dried before use by distillation over calcium hydride. p-toluenesulfonyl azide was obtained from p-toluenesulfonyl chloride and sodium azide in ethanol, following the procedure of Curtius [1]. Di-p-toluenesulfonamide and its sodium salt was prepared according to the method of Dykhanov [21] with p-toluenesulfonamide and p-toluenesulfonyl chloride in aqueous sodium hydroxide.

Sodium Salt of p-Toluenesulfonamide

A mixture of p-toluenesulfonamide and the sodium salt of p-toluenesulfonamide in dimethyl sulfoxide was generated in situ by the slow addition of an excess of p-toluenesulfonamide in dimethyl sulfoxide to a stirred solution of dimsyl anion under nitrogen. Dimsyl anion was prepared by treating dimethyl sulfoxide with sodium hydride (50% oil suspension) as described by Corey and Chaykovsky [40]. After addition of p-toluenesulfonamide to the dimsyl anion the solution was stirred for 2.5 h at 60°C under nitrogen. This solution was cooled to room temperature before further use.

Isolation of a Mixture of 1,2 and 3-^{15}N-Labeled I

Dimethyl sulfoxide solutions of ^{15}N-labeled p-toluenesulfonyl azide scrambled by p-toluenesulfonamide anion or azide ion were combined. After addition of water to the solution, it was extracted three times with pentane. The combined pentane extracts were washed three times with water, dried first over anhydrous sodium sulfate, then over calcium sulfate. The solvent was removed under reduced pressure, and the ^{15}N spectrum of the residual mixture of ^{15}N-labeled p-toluenesulfonyl azides showed that no other ^{15}N-labeled compounds were present.

Reactions of di-p-Toluenesulfonamide with Sodium Azide

Di-p-toluenesulfonamide (5.5 g. 0.017 moles) and 3.0 g (0.46 moles) of sodium azide were added to 80 ml of dimethyl sulfoxide. The mixture was stirred at room temperature for 4 days. After addition of 400 ml water, the solution was extracted with pentane. The combined extracts were washed twice with water, dried over anhydrous sodium sulfate, and the solvent removed under reduced pressure. The remaining faint-yellow residue was dissolved in ether and an ethereal solution of triphenylphosphine was added. No p-toluenesulfonyl azide triphenylphosphine adduct could be isolated [41].

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SECTION 3

THE REACTION OF p-TOLUENESULFONYL AZIDE WITH POTASSIUM AZIDE

INTRODUCTION

In Section 2 it was reported that p-toluenesulfonyl azide (I) formally transfers an azido group to azide ion in dimethyl sulfoxide to give p-toluenesulfinate anion and dinitrogen (Eq. 1).

$$TsN_3 + N_3^- \longrightarrow Ts^- + 3N_2 \qquad (1)$$

This reaction bears a strong formal resemblance to halogen-exchange reactions [1], where sulfinate ion and azide are regarded as pseudohalides (Eq. 2).

$$TsN_3 + N_3^- \longrightarrow Ts^- + (N_3)_2 \qquad (2)$$

In this case, the pseudohalogen $(N_3)_2^2$, is not stable and decomposes to dinitrogen.

The reaction of I with potassium azide-1-^{15}N has been reexamined in toluene and dichloromethane by ^{15}N NMR. Azide ion exchange (3), leading to I-1-^{15}N, and I-3-^{15}N, occurs in these solvents, just as it does in dimethyl sulfoxide.

$$TsN_3 + {}^{15}N{=}N{=}N^- \longrightarrow Ts{-}{}^{15}N{=}N{=}N + Ts{-}N{=}N{=}{}^{15}N + N_3^- \qquad (3)$$

Curiously, in dichloromethane and toluene, the formation of I-2-^{15}N is also indicated (4).

$$TsN_3 + {}^{15}N{=}N{=}N^- \longrightarrow Ts{-}N{=}{}^{15}N{=}N + N_3^- \qquad (4)$$

Two mechanisms for this scrambling are proposed in this section. Azide-ion metathesis (Eq. 5) involving reversible formation of an N-pentazole derivative (II) followed by reaction 3 could account for the ^{15}N-label at the central nitrogen of I.

$$TsN_3 + N{=}N{=}{}^{15}N^- \rightleftharpoons Ts{-}\bar{N}{-}N_4({}^{15}N) \rightleftharpoons TsN_3 + N{=}{}^{15}N{=}N^- \qquad (5)$$

II

Alternatively, a scrambling route involving reversible addition of p-toluenesulfonylnitrene to I can be envisioned (6)

$$TsN{:} + {}^{15}N{=}N{=}N{-}Ts \longrightarrow Ts{-}\dot{N}{-}{}^{15}N{=}N{-}\dot{N}{-}Ts \longrightarrow Ts{-}N{=}{}^{15}N{=}N + {:}NTs \qquad (6)$$

These mechanisms, and the evidence for them will be described in detail later. In addition, the reaction of I with potassium azide-1-^{15}N in dichloromethane in the presence of iodide ion is examined.

RESULTS AND DISCUSSION

The Reaction of I with Potassium Azide-1-^{15}N in Dimethyl Sulfoxide

Although reaction 3 occurs in relatively dilute dimethyl sulfoxide solutions, reaction 4 does not. The ^{15}N NMR of a more concentrated solution of unlabeled I and potassium azide-1-^{15}N in dimethyl sulfoxide is shown in Fig. 1. the signals of I-3-^{15}N at 132.2 ppm and I-1-^{15}N at 234.0 ppm are visible in equimolar amounts, in accord with azide ion exchange (Eq. 3). Terminally labeled azide ion is visible at 270.5

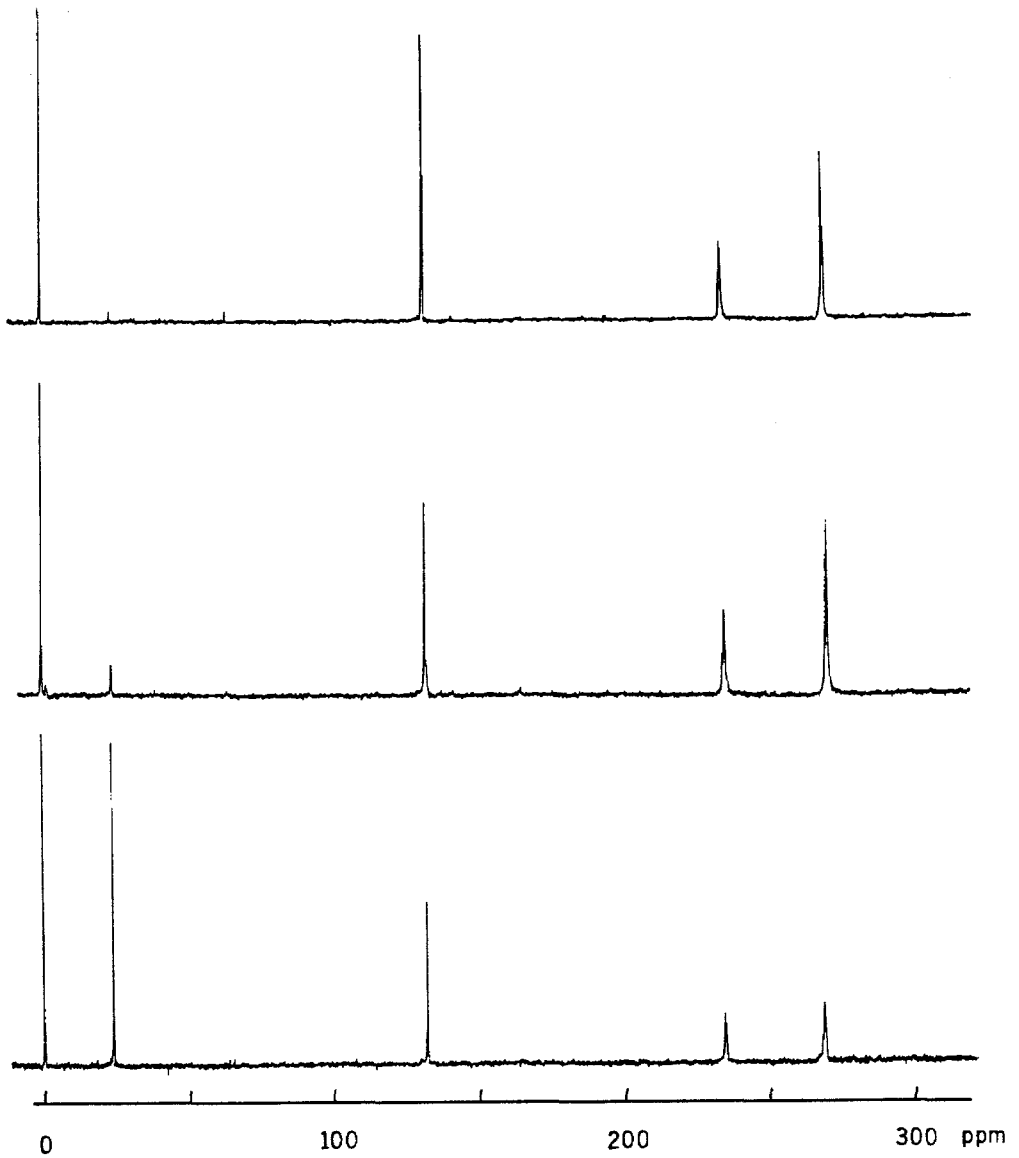


Figure 1. ^{15}N spectra of 4.8×10^{-3} mol potassium azide-1-^{15}N, 1.0×10^{-2} mol p-toluenesulfonyl azide in 20 ml dry dimethyl sulfoxide, 20 μsec pulse, 10-sec repetition rate. Spectrum of sample (a) immediately after preparation, 2109 transients; (b) 12 hours after preparation, 3719 transients; (c) two weeks after preparation, 1955 transients.

ppm. Resonances due to ^{15}N-labeled dinitrogen (64.2 ppm) and di(p-toluenesulfonyl) triazenyl anion (24.2 ppm) are visible in Fig. 1a, consistent with reaction 1 followed by reaction 7.

$$TsN_3 + Ts^- \longrightarrow Ts-\bar{N}-N=N-Ts \qquad (7)$$

There are no signals corresponding to ^{15}N-label in the central nitrogen of I (142.2 ppm) or azide ion (125.8 ppm) in Fig. 1. Thus the scrambling of Equation 4 does not occur in this more concentrated solution, even after two weeks (Fig. 1c).

The Reaction of I with Potassium Azide-1-^{15}N in Toluene

The ^{15}N NMR of a mixture of I and potassium azide-1-^{15}N in toluene is shown in Fig. 2. A large excess of 18-crown-6 was added to the sample to partially solubilize the solid potassium azide. [3a] The ^{15}N signals due to label at N1 and N3 of p-toluenesulfonyl azide are visible at 236.2 and 133.5 ppm, in accord with fast azide exchange (Eq. 3).

The concentration of dissolved potassium azide-1-^{15}N is small and dissolution is slow. The ^{15}N signal assigned to dissolved potassium azide-1-^{15}N at 275.0 ppm is visible only after 8 hours (Fig. 2b). Curiously, an ^{15}N NMR of a potassium azide-1-^{15}N/18-crown-6 mixture [3b] shows two signals: one at 256.6 ppm and the other at 274.2 ppm. After several days the signal at 256.6 moves to 254.4 ppm and the 274.2 ppm signal disappears [3b].

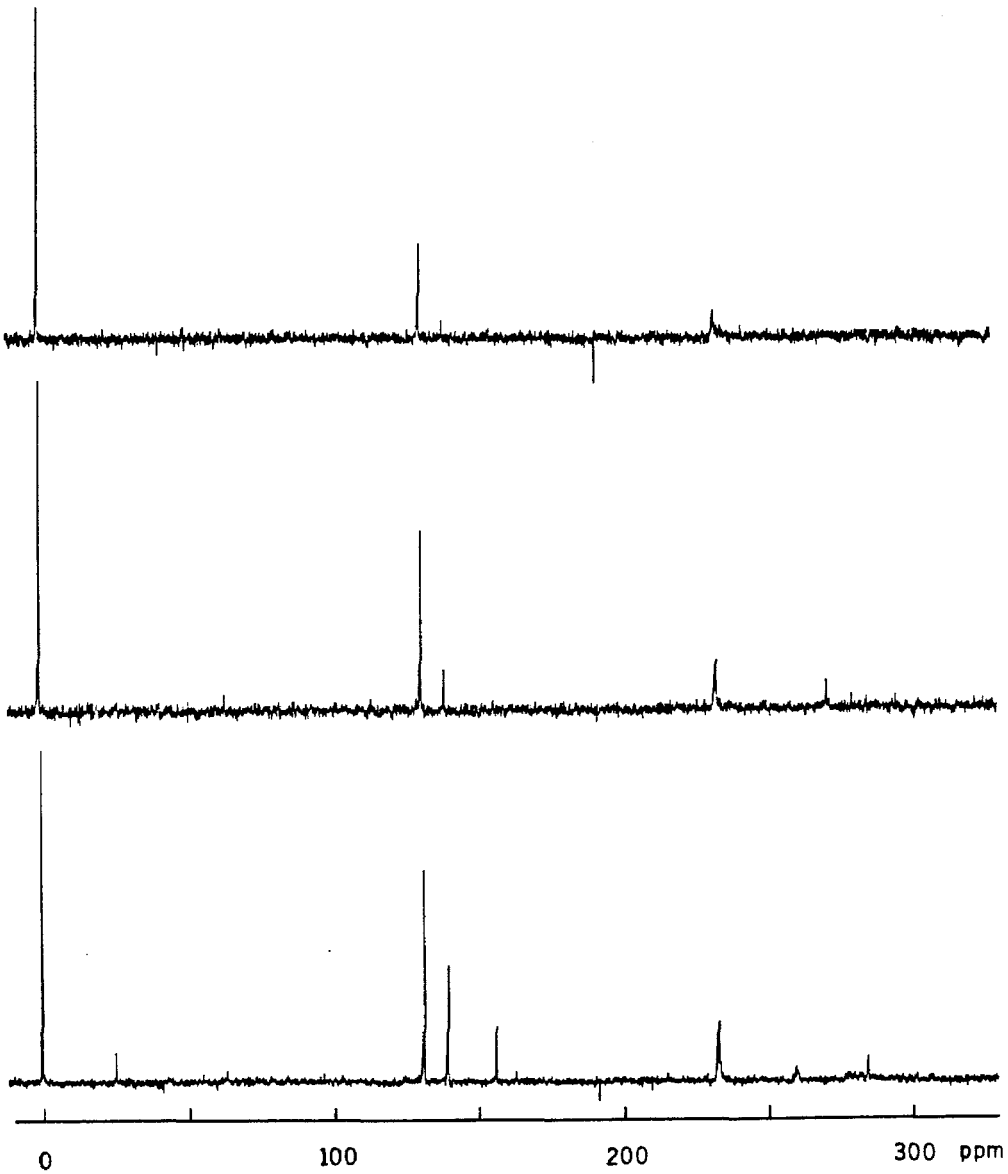
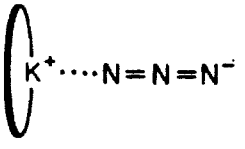
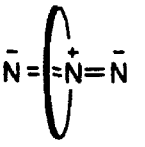


Figure 2. ^{15}N spectra of 5.2×10^{-3} mol potassium azide-1-^{15}N 1.0×10^{-2} mol I and 6×10^{-2} mol 18-crown-6 in 20 ml toluene; 20 μsec pulse, 10-sec repetition rate. Spectrum of sample (a) immediately after preparation, 2554 transients;(b) 8 hours after preparation, 3611 transients;(c) 30 days after preparation, 4802 transients.

The ^{15}N signal at approximately 275 ppm in toluene has a chemical shift closer to that of azide ion in pure water (275.8) than in a non-hydrogen-bonding solvent like dimethyl sulfoxide (270.5 ppm). This may indicate that the 275 ppm signal is due to azide ion-1-^{15}N associated with water impurity present in solution. The compound tentatively assigned to the water-associated azide ion appears to be converted to another symmetrical species with an ^{15}N signal at about 255 ppm. The observation that, as the 255 ppm signal grows the 275 ppm signal disappears even though there is an excess of solid potassium azide present, may indicate that the new compound is also associated with water. Possible candidates for this new species include fast-exchanging contact ion pairs (III) [4] and an unprecedented [5] crown-azide ion complex (IV).



III



IV

The chemical shifts of III and IV might be expected to be dependent on the relative concentration of water in solution.

The spectrum of p-toluenesulfonyl azide (I) and potassium azide-1-^{15}N in toluene-crown ether after 30 days (Fig. 2c) shows no 275 ppm resonance. A rather broad signal at 263.6 ppm is visible,

which appears to move to 257.3 ppm after 20 more days. This roaming signal is assigned to the unknown azide ion complex.

The formation of I-2-^{15}N occurs readily in this solvent mixture. After approximately 8 hours (Fig. 2b) about 5% of I is ^{15}N labeled at N2 (141.8 ppm). The potassium azide-2-^{15}N concentration is too low to permit observation of its ^{15}N signal.

Azido transfer by I to azide ion (Eq. 1) is indicated by the presence of ^{15}N-labeled molecular nitrogen (65.2 ppm) in Fig. 2b and 2c. A signal at 26.1 ppm appears in Fig. 2c which can be assigned to di(p-toluenesulfonyl) triazenyl anion, formed by reaction 7.

The signals at 158.6, 165.6 and 289.3 ppm present in Fig. 2c are unassigned.

The Reaction of I with Potassium Azide-1-^{15}N in Dichloromethane

The reaction of p-toluenesulfonyl azide (I) with azide ion was investigated in dichloromethane. The potassium azide-1-^{15}N was completely dissolved by complexation with 18-crown-6. The ^{15}N spectra of this sample are shown in Fig. 3. Equimolar amounts of I-1-^{15}N (236.5 ppm) and I-3-^{15}N (133.3 ppm) are visible in Fig. 3a, which indicates fast azide exchange (reaction 3). The terminal nitrogen of azide ion is visible at 275.8 ppm. The signals at 154.0 and 295.6 ppm result from a product of a side reaction of the azide ion with solvent and will be discussed later. Within five days (Fig. 3b) no azide ion remains and about 7% of I is labeled at the central nitrogen.

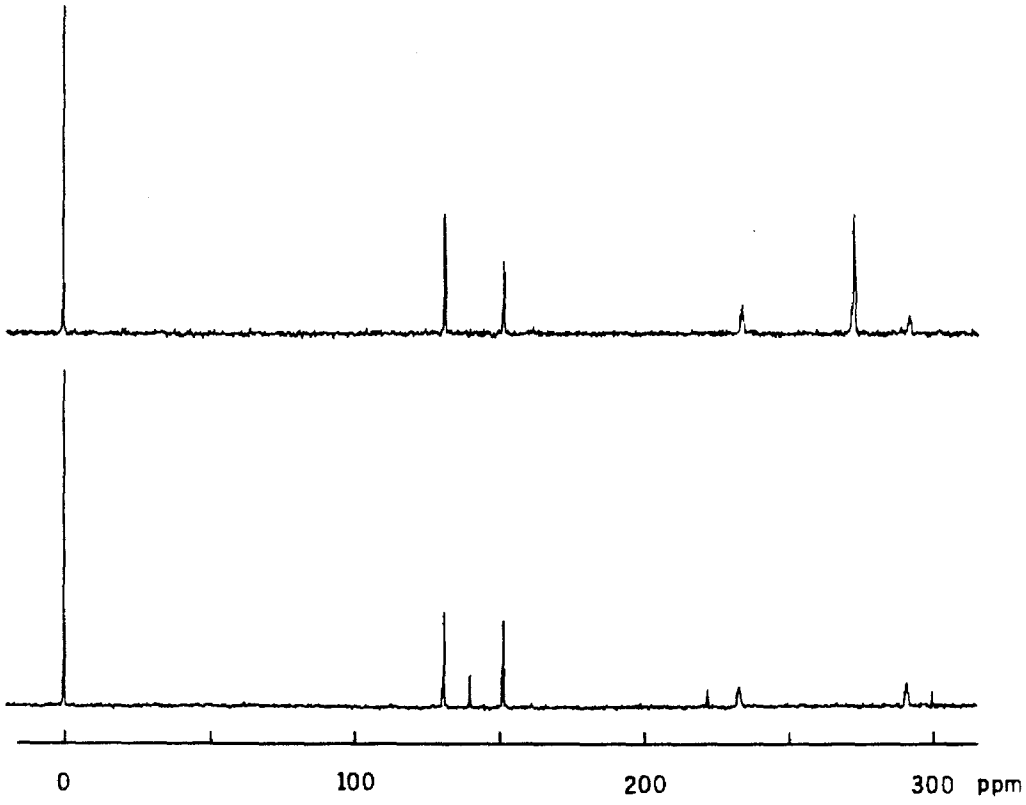


Figure 3. ^{15}N spectra of 5.9×10^{-3} mol potassium azide-1-^{15}N, 6.1×10^{-3} mol I, 6.7×10^{-3} mol 18-crown-6 in 30 ml dichloromethane; 20 μsec pulse, 10-sec repetition rate. Spectrum of sample (a) immediately after preparation, 3748 transients;(b) five days after preparation, 5213 transients.

Surprisingly, no labeled molecular nitrogen or di(p-toluenesulfonyl)-triazenyl anion signals can be seen in Fig. 3. Thus it appears that reaction 1, the azido transfer to azide ion to give p-toluenesulfinate and dinitrogen, does not occur in this solvent system.

The Reaction of Potassium Azide-1-^{15}N with Dichloromethane

Potassium azide-1-^{15}N solubilized by complexation with 18-crown-6 reacts with dichloromethane to give a product with ^{15}N signals at 154.0 and 295.1 ppm (Fig. 4a). These chemical shifts are similar to the ^{15}N shifts recently reported for methyl azide (166.9, 317.1). [6] The ^{15}N chemical shifts along with a positive test for free chloride ion suggest that azide ion displaces chloride ion from the solvent to give a chloromethyl azide or diazidomethane (Eq. 8-9).

$$CH_2Cl_2 + N_3^- \longrightarrow CH_2ClN_3 + Cl^- \quad (8)$$

$$CH_2Cl_2 + 2N_3^- \longrightarrow CH_2(N_3)_2 + Cl^- \quad (9)$$

Neither of these azides appears to have been previously reported, but the diazidomethane formed in reaction 9 is undoubtedly highly explosive [7]. Considering the large excess of dichloromethane, reaction 9 seems somewhat unlikely, although the chlorine of chloromethyl azide is expected to be displaced in an S_N2-type reaction more easily than a chlorine of dichloromethane.

The chloromethyl azide does not undergo fast azide exchange.

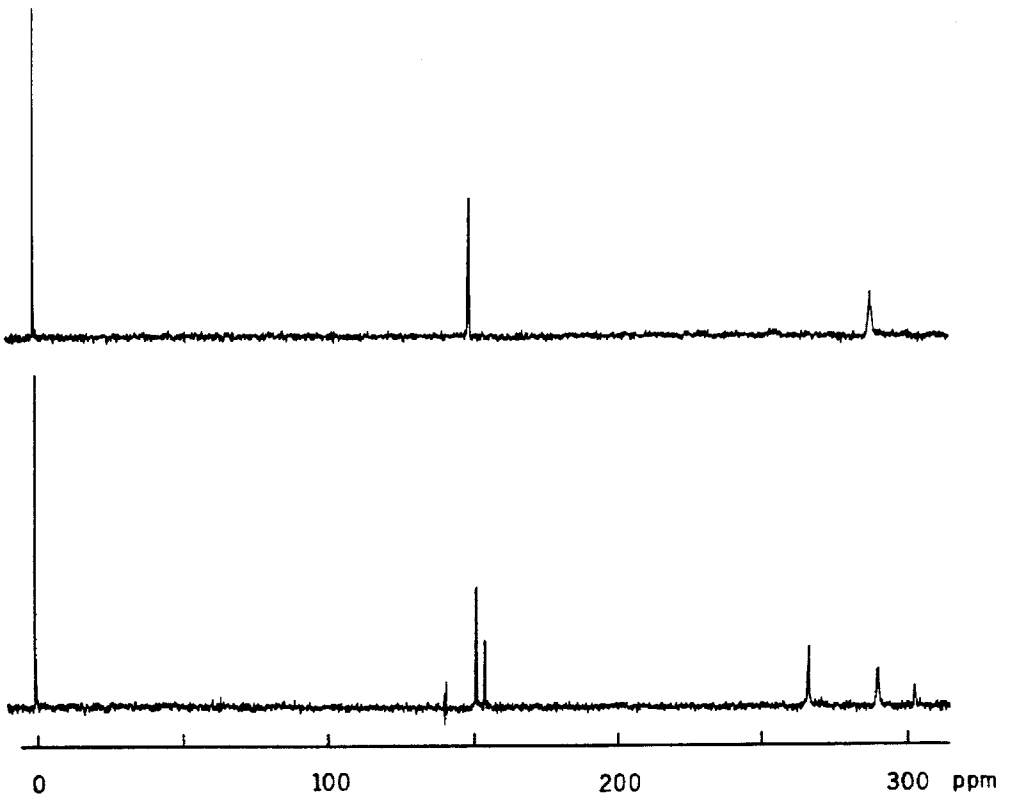


Figure 4. (a) ^{15}N spectrum of a solution of chloromethyl azide generated in situ from 3.4×10^{-3} mol potassium azide-1-^{15}N, 2.5 g 18-crown-6 in 20 ml dichloromethane, 20 μsec pulse, 10-sec repetition rate, 1831 transients. (b) ^{15}N spectrum of a solution of chloromethyl azide (generated in situ from 3.4×10^{-3} mol potassium azide-1-^{15}N, 3.4×10^{-3} mol potassium azide, 5.0 g 18-crown-6 in 20 ml dichloromethane) after addition of 3×10^{-3} mol of the sodium salt of p-toluenesulfinic acid, dihydrate and 5.0 g 18-crown-6. 20 μsec pulse, 10-sec repetition rate, 4059 transients.

This was shown by the addition of natural abundance potassium azide to a solution of ^{15}N-labeled chloromethyl azide (10)

$$CH_2Cl^{15}N_3 \; + \; N_3^- \; \not\longrightarrow \; CH_2ClN_3 \; + \; ^{15}N_3^- \qquad (10)$$

No ^{15}N-labeled potassium azide was visible in the ^{15}N NMR spectrum of this solution. This explains why there is no resonance assignable to ^{15}N-label at the central nitrogen of chloromethyl azide in Fig. 3b.

The Reaction of p-Toluenesulfinate Ion with Chloromethyl Azide in Dichloromethane

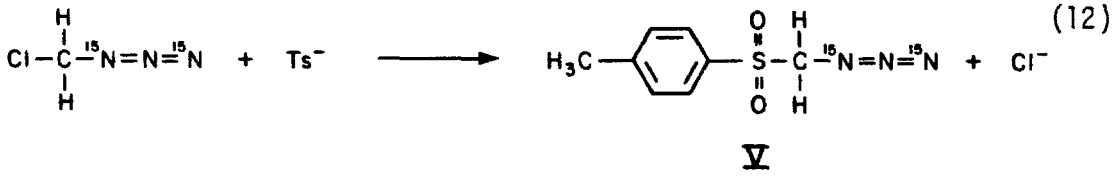
Having generated an ^{15}N-labeled alkyl azide in situ, the possibility of its reaction with p-toluenesulfinate anion to give a triazenyl anion was investigated. To do this, 0.5 equivalents of the sodium salt of p-toluenesulfinic acid (dihydrate) was added to the chloromethyl azide in dichloromethane (Fig. 4b). Gas was visibly evolved. The expected reaction (Eq. 11) did not appear to occur.

$$Cl-CH_2-N_3 \; + \; Ts^- \; \longrightarrow \; Cl-CH_2-N=N-\bar{N}-Ts \qquad (11)$$

The ^{15}N NMR of the solution (Fig. 4b) showed resonances at 65.2, 157.6, 271.2 and 308.4 ppm, in addition to the signals of the chloromethyl azide (154.7 and 295.6 ppm). The ^{15}N signals at 65.2

and 271.2 ppm are assigned to ^{15}N-labeled dinitrogen and p-toluenesulfonamide anion [8], respectively. The signals at 157.6 and 308.4 ppm are assigned to ^{15}N-labeled γ and α nitrogens of a new alkyl azide.

A mechanistic scheme which is consistent with these assignments is outlined below. The first step involves the reaction of p-toluenesulfinate at the carbon of chloromethyl azide rather than the terminal nitrogen (Eq. 12). Presumably the azido group of chloro methyl azide is not electrophilic enough to couple with p-toluenesulfinate as in reaction 11, or reaction 11 is sufficiently reversible that the irreversible S_N2 reaction diverts the triazenyl anion to other products.

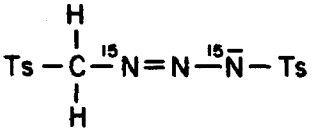


(12)

V

Based on hard and soft acid-base arguments, p-toluenesulfinate is expected to be alkylated at sulfur [9] to give the known α-azido sulfone[10] (V), rather than at oxygen to give a sulfinate ester. The signals at 157.6 and 308.4 in Fig. 4b are reasonably assigned to the expected sulfone V.

In contrast to the triazenyl anion formed by reaction 11, the triazenyl anion (VI) formed by the coupling of V with p-toluenesulfinate, possesses a relatively acidic α-hydrogen [11].



VI

VI is expected to tautomerize, and the resulting triazene should decompose to give a diazo compound and p-toluenesulfonamide anion (Eq. 13)

(13)

Because p-toluenesulfinate was added in the form of the dihydrate, the known p-toluenesulfonyldiazomethane [12] will hydrolyze to give the α-hydroxy and α-chloro sulfone and dinitrogen [12b]. These reactions explain the presence of ^{15}N-labeled p-toluenesulfonamide anion and molecular nitrogen in Fig. 4b.

VI is identical to the intermediate expected from the diazo-transfer by p-toluenesulfonyl azide (I) to the carbanion of p-toluenesulfonyl methane. Although di(p-toluenesulfonyl) diazomethanes can be prepared by the reaction of di(p-toluenesulfonyl) methanes with I and alkali, monosulfonyldiazomethanes cannot [13]. These preliminary studies suggest that the addition of p-toluene-sulfinate anion to electrophilic azides possessing an α-hydrogen might be a new and useful entry onto the standard diazo-transfer surface.

The Reaction of I with Potassium Azide-1-^{15}N in the Presence of Potassium Iodide

The ^{15}N spectrum of an equimolar solution of I, potassium azide-1-^{15}N, potassium iodide in dichloromethane/18-crown-6, is markedly different from Fig. 3. Azide exchange and formation of chloromethyl azide is observed, but in the presence of iodide ion, I-2-^{15}N is not formed. In contrast to ^{15}N-spectra in the absence of iodide ion, a strong signal due to ^{15}N-labeled molecular nitrogen (65.3 ppm) is visible immediately after sample preapration. Molecular iodine is also formed under these conditions.

We propose that the iodine and molecular nitrogen are products from the reactions of an intermediate iodoazide [14]. Control experiments indicate that in dichloromethane, iodine is not formed from a direct reaction of I and iodide. Azide ion is apparently required as a catalyst (Eq. 14).

$$TsN_3 + N_3^- + I^- \longrightarrow Ts^- + N_3^- + IN_3 \qquad (14)$$

The iodoazide formed in reaction 14 is expected to react with azide ion to give dinitrogen (Eq. 15):

$$IN_3 + N_3^- \longrightarrow I^- + 3N_2 \qquad (15)$$

or iodide to give iodine (Eq. 16):

$$IN_3 + I^- \longrightarrow I_2 + N_3^- \qquad (16)$$

Analogous reactions have been observed with bromoazide.[15] Dübgen and Dehnicke[16] have recently reported the low temperature isolation of iodoazide complexes from the reaction of iodoazide with tetramethylammonium iodide or azide (Eq. 17-18).

$$IN_3 + NMe_4I \longrightarrow NMe_4[I(IN_3)] \quad (17)$$

$$IN_3 + NMe_4N_3 \longrightarrow NMe_4[I(N_3)_2] \quad (18)$$

Interestingly, the reaction of I_2 with azide ion, thought at one time only to occur in the presence of certain sulfur-containing catalysts [17], was found by Dübgen and Dehnicke [16] to yield the iodine-iodoazide complex. Thus reaction 16 may be reversible.

Reaction 14, if it occurs, requires the formation of p-toluenesulfinate anion. Just as observed for the conditions of the spectrum shown in Fig. 3, no di(p-toluenesulfonyl) triazenyl anion or the products from the reaction of the sulfinate with chloromethyl azide are visible in the presence of iodide. Control experiments show that di(p-toluenesulfonyl) triazenyl anion is formed on treatment of I with the sulfinate salt (dihydrate) in dichloromethane/crown ether. The formation of the triazenyl anion, however, is expected to be reversible. Thus either reaction 14 does not occur, or the p-toluenesulfinate anion is consumed in one or more fast and irreversible reactions.

A likely route for the disappearance of p-toluenesulfinate anion

is its known reaction with iodine (Eq. 19) [18].

$$Ts^- + I_2 \longrightarrow TsI + I^- \qquad (19)$$

This reaction alone is not enough to account for the lack of ^{15}N-labeled products derived from p-toluenesulfinate. But reaction (19) coupled with the nucleophilic attack by p-toluenesulfinate on p-toluenesulfonyl iodide [19] should be sufficient to keep the p-toluene sulfinate anion concentration low.

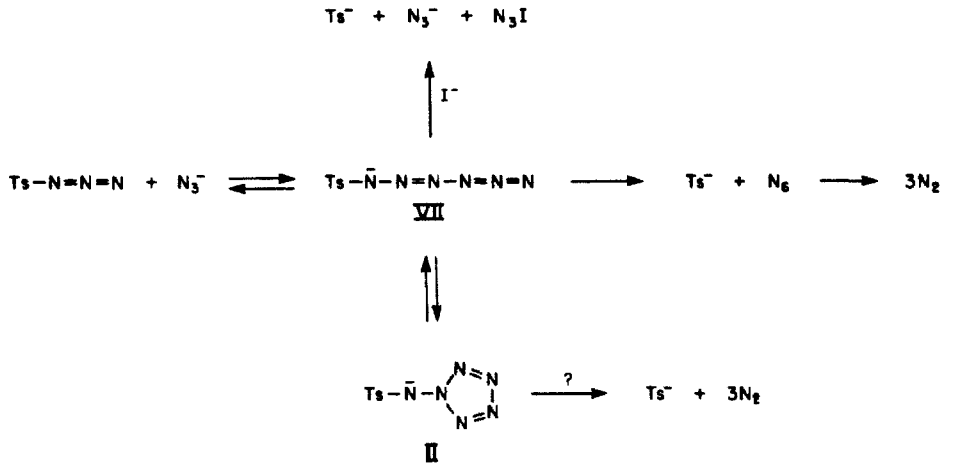
Mechanism of the Formation of I-2-^{15}N: Azide-Ion Metathesis

Reversible coupling of I with terminally ^{15}N-labeled azide ion to give an intermediate p-toluenesulfonylpentazole anion (II) could account for formation of scrambled azide ion (Eq. 5). Azide exchange with I (Eq. 3) would then afford I-2-^{15}N. There are many cases of hetereocummulenes reacting with azide ion or hydrazoic acid to form stable five-membered ring hetereocycles. Examples include the reactions of isothiocyanates [20] and thioketenes [21] with hydrazoic acid to give thiatriazoles, the reactions of hydrazoic acid with carbodiimides [22] and ketenimines [23] to give tetrazoles, and the coupling of carbon disulfide [24] with azide ion to give 1,2,3,4-thiatriazolinethionate anion.

The inhibition of I-2-^{15}N formation by iodide in dichloromethane,

however, suggests that the N-pentazole (II) derivative is actually formed by the cyclization of a linear p-toluenesulfonylhexazenyl anion (VII) [25]. The iodide ion appears to intercept the hexazine derivative, inducing decomposition to p-toluenesulfinate anion, azide ion and iodoazide, before cyclization can occur. The suggested mechanism is outlined in Scheme 1.

Scheme 1

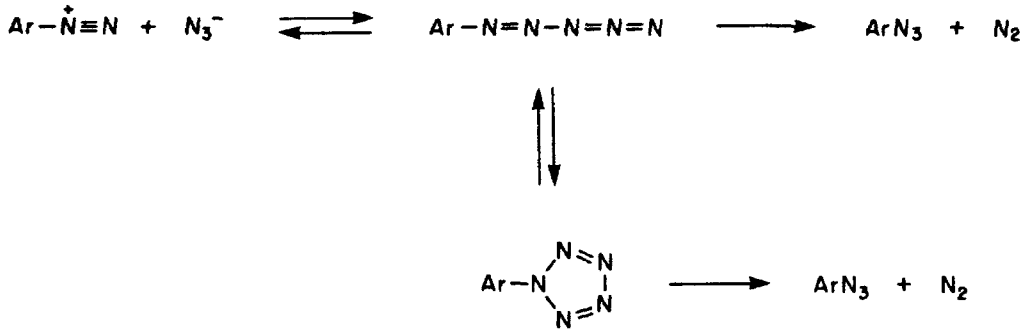


The decomposition route of VII is strongly dependent on solvent. In dimethyl sulfoxide, VII decomposes to p-toluenesulfinate anion and molecular nitrogen. In toluene, the substituted hexazene (VII) seems long-lived enough for reversible cyclization to II to compete with decomposition. In dichloromethane, however, only the reversible cyclization appears to occur. In this solvent the cyclization is effectively prevented by addition of potassium iodide. The origin of the large solvent effect on the mechanism is not understood, but

polarity and basicity of the solvent may be involved.

The reactions of Scheme 1 are related to the reactions of aryldiazonium salts with azide ion. The existence of a similar ring-chain equilibrium has been established by ^{15}N-labeling and kinetic evidence (Scheme 2) [26].

Scheme 2

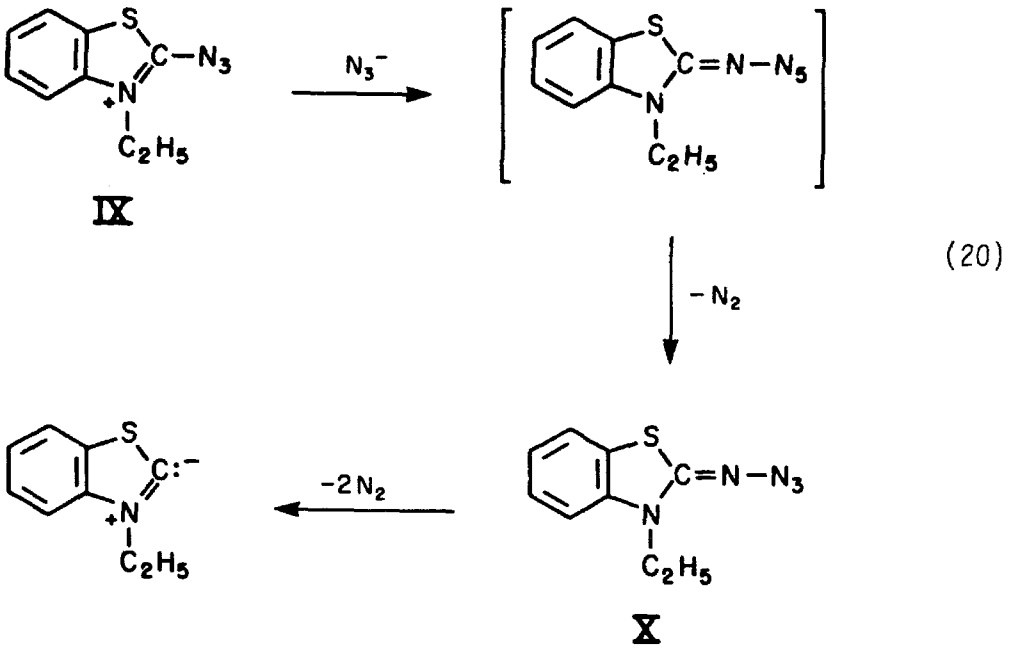


VIII

It is not clear if the arylpentazole (VIII) is formed directly from the aryldiazonium salt and azide ion, or by cyclization of the arylpentazene. Arylpentazole (VIII) intermediates have been isolated and characterized spectroscopically [27].

There have also been several studies concerning the reaction of azides with azide ion. Both azide exchange [28] and reaction at the terminal nitrogen have been observed.

Balli has examined the reaction of hetereocyclic azidinium salts with azide ion. Not surprisingly, the N-diazonium salts [29] react with azide ion to give N-azides, presumably via a substituted hexazene (Eq. 20) [30].



(20)

The N-azide (X) is stable at low temperature, but loses two molecules of nitrogen at room temperature to afford an ylide [30]. Here, ^{15}N-labeling experiments were used to demonstrate that azide exchange with IX also occurs [30].

Inorganic examples of azido transfer to azide ion have been reported. Most notable is the reaction of bromoazide with azide ion in aqueous solution (Eq. 21) [15].

$$BrN_3 + N_3^- \longrightarrow Br^- + 3N_2 \qquad (21)$$

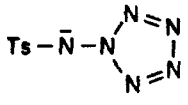
Mechanism of the Formation of I-2-^{15}N: p-Toluenesulfonylnitrene

Another way in which I-2-^{15}N might be formed is via a chain reaction of p-toluenesulfonylnitrene with I-3-^{15}N (Eq. 6) [31] through the intermediacy of a di-(p-toluene)sulfonyltetrazadiene (XI) [32].

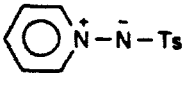
XIa XIb

Transition metal complexes of XI are in fact known [33] and are thought to be formed by the addition of a metal-bound p-toluenesulfonylnitrene to p-toluenesulfonyl azide (I).

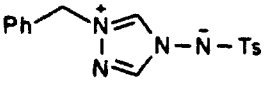
One possible source of p-toluenesulfonylnitrene in the presence of I and azide ion, is the decomposition of the N-pentazole derivative (II) discussed in Scheme 1. II resembles ylides XII [34] and XIII[35], which have both been investigated as potential p-toluenesulfonylnitrene precursors.



II

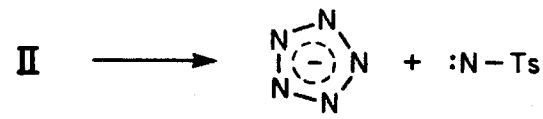


XII



XIII

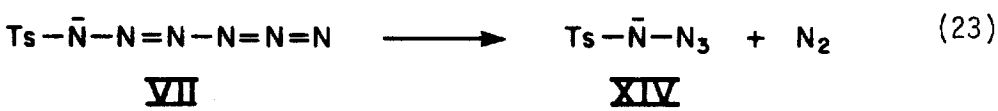
The decomposition of II could give p-toluenesulfonylnitrene and the unknown pentazole anion (Eq. 22). [27]



(22)

Once formed, the pentazole anion could quickly decompose to azide ion and molecular nitrogen by a symmetry allowed cycloreversion [36].

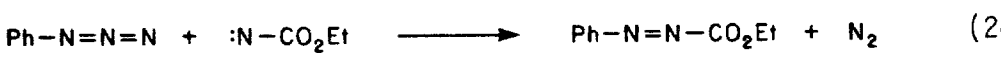
Another potential p-toluenesulfonylnitrene precursor is the N-azide derivative (XIV) formed by loss of nitrogen from p-toluenesulfonylhexazenyl anion (VII)



(23)

This reaction is related to the stepwise decomposition of X (Eq. 20)[30]. Elimination of azide ion from XIV would clearly give p-toluenesulfonylnitrene.

The proposed attack of p-toluenesulfonylnitrene on the terminal nitrogen of p-toluenesulfonyl azide (I) to give XIII is somewhat unusual, because singlet p-toluenesulfonyl nitrenes are highly electrophilic [31] and should prefer the α-nitrogen of I. Indeed, Gibson and coworkers [37] have isolated phenylazocarboxylate from the reaction of phenyl azide with singlet ethoxycarbonylnitrene, a product consistent with α-attack by the nitrene (Eq. 24).



(24)

It is, however, quite possible that the anionic nitrene precursors (II,XIV) are somewhat more nucleophilic than the free nitrene and that it is these complexes that attack the terminal nitrogen of I. The nitrenoid chloramine-T, a reasonable model for XIV, does in fact behave as a nucleophile in some cases [38].

If reaction 6 occurs, the reaction of p-toluenesulfonylnitrene (or a complex thereof) with I-1-^{15}N (formed in reaction 3) will afford the ^{15}N-labeled nitrene (25).

$$Ts-{}^{15}N=N=N \quad + \quad :N-Ts \longrightarrow Ts-{}^{15}N: \quad + \quad N=N=N-Ts \qquad (25)$$

Thus, products from the insertion of the singlet nitrene [39] into the C-H bonds of the solvent or crown ether should be visible in the ^{15}N NMR. Examination of a sample of I and potassium azide-1-^{15}N in toluene/18-crown-6 fifty days after preparation by ^{15}N NMR, reveals a small doublet at 283.9 ppm (J=86 Hz) and a singlet at 289.3 ppm. ^{1}H-decoupling experiments show that these nitrogens possess a strong negative NOE. These signals are too far upfield to correspond to the sulfonamides [40] expected from nitrene insertion into the toluene C-H bonds. However, because of a lack of ^{15}N-shifts for suitable model compounds, the product of nitrene insertion into the C-H bond of 18-crown-6 cannot be ruled out.

CONCLUSION

In summary, evidence for the addition of azide ion to p-toluenesulfonyl azide (I) forming a discrete addition intermediate has been presented. In dimethyl sulfoxide this intermediate, the p-toluenesulfonylhexazenyl

anion (VII), decomposes to p-toluenesulfinate anion and molecular nitrogen. In dichloromethane and toluene, I-2-^{15}N is formed from the reaction of I with terminally ^{15}N-labeled azide ion solubilized by 18-crown-6. Two mechanisms for this scrambling have been proposed. In the first mechanism, VII is reversibly formed, and can reversibly cyclize to an N-pentazole derivative. The ^{15}N-label at N2 of I is derived from azide exchange with azide ion scrambled in this way. In the second mechanism, I-2-^{15}N is formed by chain reaction of p-toluenesulfonylnitrene with I-3-^{15}N. The anionic nitrene precursors are derived from the initially formed p-toluenesulfonylhexazenyl anion. Iodide ion prevents the formation of I-2-^{15}N in dichloromethane by inducing the decomposition of the hexazene derivative before further reaction can occur. More study is needed to unravel the mechanistic details of this novel reaction of azide ion with I.

EXPERIMENTAL

The ^{15}N NMR spectra were taken at 18.25 MHz with a Bruker WH-180 spectrometer, using 15-25 ml samples in 25-mm sample tubes. A 5-mm concentric tube containing a solution prepared by dissolving sufficient $H^{15}NO_3$ in D_2O to give a 1-M acid concentration provided lock and reference signals. Chemical shifts are reported in ppm upfield from external HNO_3. All spectra were proton-coupled, and observations were made at ambient probe temperature, which was approximately 22°C.

p-Toluenesulfonyl azide was synthesized following the procedure of Curtius [41]. Potassium azide-1-^{15}N (97.2-99.5%) was obtained from

Prochem. 18-crown-6 was purchased from Aldrich Chemical Co. and used without purification. Dimethyl sulfoxide was sequentially dried over 3 Å molecular sieves and toluene fractionally distilled before use. Commercially available spectrophotometric grade dichloromethane was employed in these studies.

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Perkins. Their help is gratefully acknowledged.

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$$ArSO_2O\overset{O}{\overset{\|}{S}}-Ar + ArSO_2^- \longrightarrow ArSO_2\overset{O}{\overset{\|}{S}}-Ar + ArSO_3^-$$

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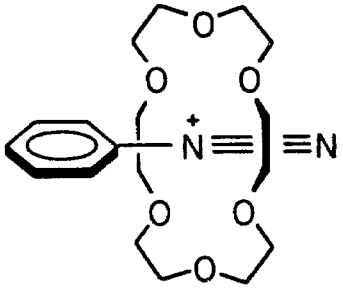
PART II

^{15}N AND ^{13}C NUCLEAR MAGNETIC RESONANCE STUDIES OF ARYLDIAZONIUM COMPOUNDS. EFFECT OF SUBSTITUENT, SOLVENT, AND 18-CROWN-6.

INTRODUCTION

Just as macrocyclic polyethers bind a wide variety of metal cations [1a] crown ethers have been found to complex several organic cations [1b]. A particular interesting example is the 18-crown-6 complexation of aryldiazonium cations in which the linear N_2^+ group is thought to insert into the hole of the macrocyle (I). [2]



I

Evidence for I includes the importance of cavity size of the crown [3], steric effects of ortho ring substituents [4], and ^1H NMR shift changes of the ortho hydrogens[5] on complexation. Recent thermodynamic work on the stability of such complexes as a function of para substituent indicates that the interaction between N_2^+ and crown is predominantly electrostatic[5]. In fact, the structure of crystalline benzenediazonium chloride might

serve as a model for the crown complex. The N_2^+ group is surrounded by four chloride ions in a planar arrangement normal to the NN axis [6].

The cation-oxygen interaction between aryldiazonium salt and crown is strong enough to solubilize the diazonium salt in non-polar solvents such as chloroform. Crown ethers have recently been exploited in phase transfer of solid aryldiazonium salts to non-polar solutions [7-9].

In addition to enhancing the solubility of aryldiazonium salts in non-polar solvents, crown ethers also exert a strong effect on the electronic structure of the cations. This has been clearly demonstrated by alterations in the spectral and chemical properties of the complexed cations. Bartsch and coworkers have shown that the crown-complexed aryldiazonium salts enjoy increased thermal [10] and photochemical stability [11] relative to the uncomplexed form. Spectroscopic changes in the cation on complexation have been observed by ^1H NMR [5], ^{13}C NMR[12], infrared [12] and UV [10,13].

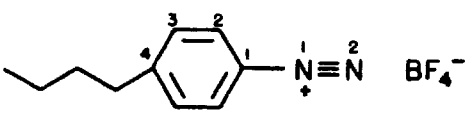
This section reports on ^{15}N and ^{13}C studies of the complexation of aryldiazonium salts by 18-crown-6. The ^{15}N resonances of the α(N1) and β(N2) nitrogens of p-tert-butylphenyldiazonium fluoborate in dichloromethane shift 5.1 ppm upfield and 1.5 ppm downfield, respectively, on addition of one equivalent of 18-crown-6. Addition of four more equivalents of 18-crown-6 shifts N1 upfield another 1.0 ppm and N2 downfield .4 ppm. In order to understand the origin of these crown-induced ^{15}N changes the effects of para substituents and solvent on the uncomplexed aryldiazonium salts were also examined.

The ^{15}N solvent shifts are found to be small, and the substituent effects are comparable to the shifts induced by 18-crown-6. In conjunction with previous spectroscopic studies, the ^{15}N and ^{13}C results indicate that the complexed aryldiazonium salt has more pure diazonium character than the uncomplexed diazonium salt.

RESULTS

Solvent Shifts

The results of the ^{13}C and ^{15}N solvent study on n-butylphenyldiazonium fluoborate (II) are presented in Table I.



II

The effects of solvent changes on nitrogen and carbon chemical shifts of II are not large. This is in accord with the reported NN stretching frequencies of aryldiazonium chlorides, which are also relatively insensitive to solvent changes [16]. Penton and Zollinger [17] have postulated that the aryldiazonium cation is only weakly solvated to explain the small influence of solvent changes on the rates of diazo coupling of p-toluenediazonium cation with N,N-dimethylaniline. The solvent effect on the rate of hetereolytic dediazoniation of benzenediazonium fluoborate is also small [18].

TABLE I. ^{15}N and ^{13}C NMR Solvent Shifts of II[a]

Solvent	$\delta N1$[b]	$\delta N2$[b]	$\delta C1$[c]	$\delta C4$[c]	B[d]
dichloromethane	143.8	58.1	110.1	160.4	43
nitromethane	143.6	58.8	110.4	160.9	59
acetonitrile	143.5	58.8	111.2	160.6	103
acetone	144.0	59.7	111.9	159.8	123
1,4-dioxane	144.4	59.9	112.2	159.5	128
dimethylformamide	143.7	60.3	112.0	161.0	166

a Corrected for diamagnetic susceptibility, reference 14.

b Upfield from external 1 M $H^{15}NO_3$ in D_2O

c Downfield from external Me_4Si.

d Lewis basicity parameter, reference 15.

Despite the small range of chemical shifts a qualitative correlation between the C1 and N2 chemical shifts of II and B^{15}, an empirical measure of solvent Lewis basicity, is observed. The terminal nitrogen shifts upfield and the C1 shifts downfield with increasing basicity of solvent. These shift changes seem to indicate some acid-base type diazonium cation-solvent interaction. The upfield shift of N2 with basic solvents is probably due to diamagnetic shielding of the terminal nitrogen by interaction with the basic solvent. The downfield shift of C1 is then very likely a consequence of reduced resonance interaction of C1 with the N_2^+ group because of the stabilization of positive charge on the β nitrogen by solvent [19]. The smaller C4 and N1 shift changes do not show a correlation with basicity of solvent. Similarly, the NN stretching frequencies are not related to solvent basicity [16].

Benzonitrile Solvent Shifts

For comparison, solvent studies on the isoelectronic benzonitrile were undertaken. Whereas the chemical shift of the terminal nitrogen of II correlates roughly with the basicity of the solvent, the chemical shift of the cyano nitrogen of benzonitrile is a function of acceptor number (AN)[20], an empirical measure of Lewis acidity, of the solvent (Table II). The upfield shifts observed in the more acidic solvents are consistent with the formation of a hydrogen-bond between the cyano lone-pair and solvent (III). [21]

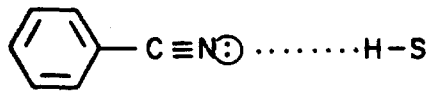
TABLE II. ^{15}N NMR Solvent Shifts of Benzonitrile [a]

Solvent	$\delta^{15}N$ [b]	AN [c]
p-dioxane	117.2	10.8
acetone	117.8	12.5
dimethylformamide	118.5	16.0
acetonitrile	119.3	18.9
dichloromethane	119.9	20.4
nitromethane	121.2	20.5
methanol	121.8	41.3

a Corrected for diamagnetic susceptibility, reference 14.

b Upfield from external 1 M $H^{15}NO_3$ in D_2O.

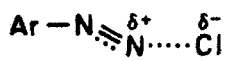
c Acceptor number, reference 20.



III

Counterion Shifts

Replacement of the fluoborate counterion of a 1.2 M solution of II in dichloromethane by chloride ion induces downfield shifts of both nitrogens. The N2 resonance changes from 58.2 to 57.4 ppm and N1 moves from 143.9 to 142.5 ppm. Infrared studies of aryldiazonium salts in acetone show that a change of counterion exerts a small effect on the NN stretching frequencies [22]. The NN stretching frequencies for the fluoborate are about 5 cm^{-1} higher than the chloride. Larger effects on the stretching frequency have been noted for other anions [23]. The decrease in NN bond order with more nucleophilic counterions has lead several workers [22,23] to propose some covalent bonding between anion and cation in salts other than fluoborates. The ^{15}N shifts of the aryldiazonium chloride is also consistent [24] with some covalent interaction between diazonium cation and chloride ion (IV).



IV

Evidence for the formation of transitory iodine and astatine aryldiazonium complexes has, in fact, recently been reported [25].

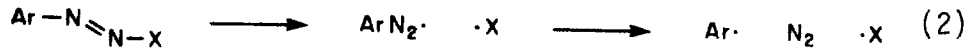
The effect of counterion on reactivity and stability of aryldiazonium salts has been widely debated and appears to be dependent on solvent and counterion. The anion of the diazonium salt in dilute solutions of H_2SO_4 and HCl has no appreciable influence on the rate of thermal decomposition [26]. The counterion also has no significant effect on the rate of azo coupling in aprotic polar solvents [17]. Evidence for ion pairing of aryldiazonium salts in non-polar solutions has recently been provided by Juri and Bartsch [5]. Stronger ion-pairing *between* BF_4^- *and* *p-t-butylbenzenediazonium cation relative to* PF_6^- was demonstrated by kinetic and ^{19}F NMR studies [5]. This is particularly remarkable considering the similarity between the two counterions.

It appears that the interaction between an aryldiazonium cation and non-nucleophilic counterions or solvents is fundamentally different than that of nucleophilic counterions or highly nucleophilic solvents. For nucleophilic anions (e.g., chloride) the interaction appears to involve a slight geometry change of the diazonium cation (1):

$$Ar-N{=}N^+ + X^- \longrightarrow Ar-N\diagdown\!\!\diagup N-X \qquad (1)$$

In the same way, but to a larger degree, highly basic solvents tend to form covalent complexes with aryldiazonium salts. Spectral evidence for pyridine and dimethylsulfoxide aryldiazonium complexes have been reported by Zollinger and coworkers [27]. Interestingly, aryldiazonium

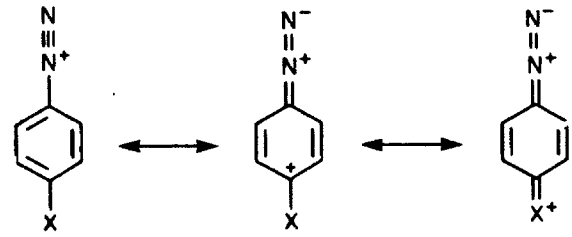
salts decompose by a homolytic mechanism in highly nucleophilic solvents, presumably by cleavage of the covalent complex (2) [18]. Halide counterions also appear to induce the homolytic decomposition of aryldiazonium salts [28].



(2)

Substituent Effects

In contrast to the small solvent effect observed, the influence of substituents on ^{13}C and ^{15}N shifts of aryldiazonium salts is substantial. ^{13}C studies by Olah and Grant [29] on substituted aryldiazonium salts have shown that resonance forms Vb and Vc contribute significantly to the ground state structure of aryldiazonium salts, particularly those with an electron donating para substituent.



Va Vb Vc

The importance of the diazo resonance structures (Vb,Vc) in delocalizing the positive charge of the N_2^+ group is also demonstrated by ^{15}N NMR. ^{15}N NMR shifts of five para-substituted aryldiazonium fluoborates in acetonitrile are listed in Table III.

The N1 resonance shifts downfield with electron-donating substituents, as expected for an increase in diazo character (Vb,Vc). [30]

TABLE III. ^{15}N NMR of Para-Substituted Diazonium Salts in Acetonitrile[a]

Substituent	Concentration(M)	δN2	δN1
MeO-	.8	51.9	140.5
(n-butyl)-	.5	57.6	142.4
H-	1.1	60.1	143.6
HO_2C-	.5	59.6	144.6
O_2N	.3	59.4	146.1

a Upfield from external 1M $H^{15}NO_3$ in D_2O.

In addition, the N1 chemical shifts correlate well with σ_p^+, indicating strong resonance interaction of the N_2^+ group with the para substituents (Fig. 1). Both the frequency [16] and logarithm of the intensity [31] of the NN stretch of aryldiazonium salts in solution correlate with the σp^+ substituent constant. The increase in intensity and decrease in frequency of the NN stretch with electron-donating substituents has also been interpreted as an increase in diazo character of the N_2^+ group [16,31].

The electronic character of N2 is also influenced by para substituents. A linear relationship between the π-electron population of N2 and σ_p^+ has been obtained by Oja and Nielsen from a Townes-Dailey analysis of ^{14}N NQR results [32].

The chemical reactivity of aryldiazonium salts is also strongly dependent on ring substituent. The equilibrium and rate of coupling of N2 with nucleophiles gives good Hammett plots against ordinary σ values [33]. The half-wave potential for the one-electron reduction of substituted aryldiazonium salts also correlates well with σ_p^+ values [34].

Curiously, the chemical shift of N2 does not correlate with σ_p^+ or σ_p (Fig. 2). The N2 resonances of salts with para groups more electron donating than H move downfield with increasing electron donation, as expected for an increase in diazo character [30], represented by structures Vb and Vc. In fact, the N2 resonances for these aryldiazonium salts are more sensitive to substituent than the N1 resonances of the same compounds. This can be taken as evidence for greater positive charge on the terminal nitrogen, in accord with the calculated

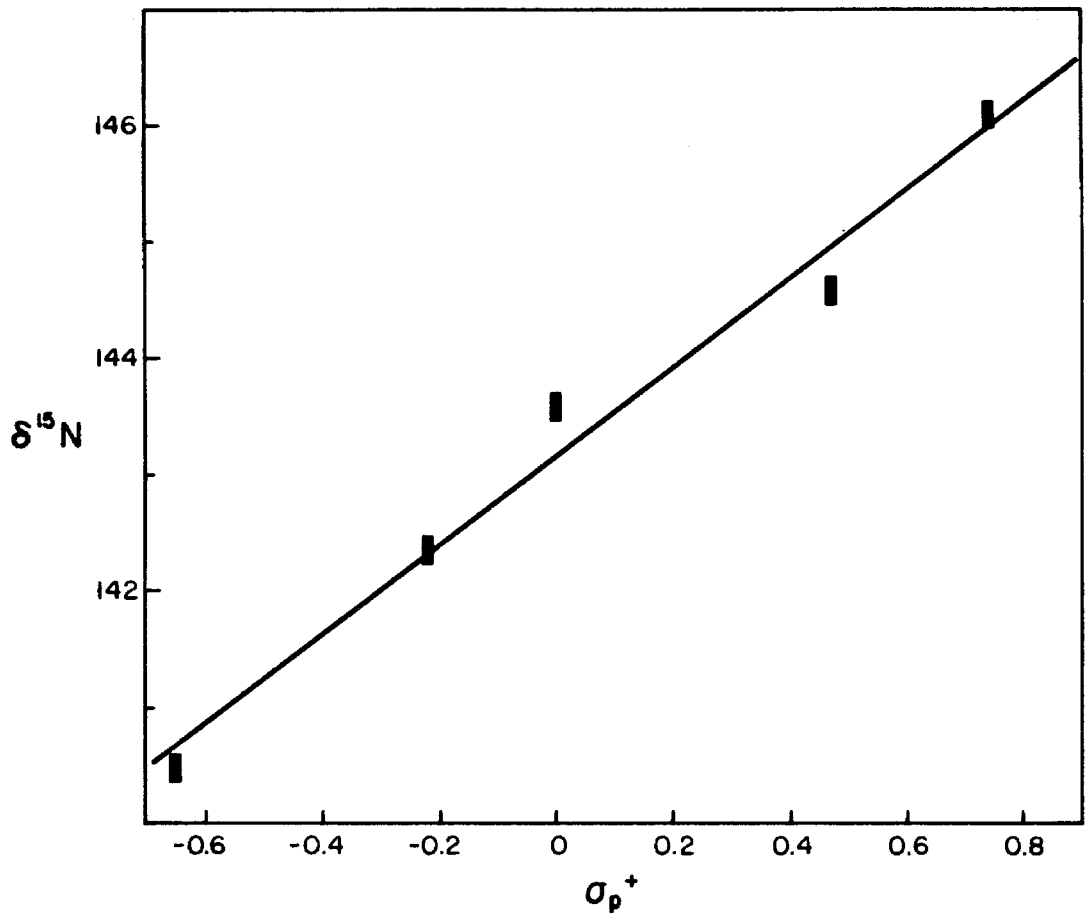


Figure 1. Plot of the N1 ^{15}N shifts of substituted aryldiazonium fluoborates against σ^+. (slope 3.83, intercept 143.2 ppm, correlation coefficient 0.979).

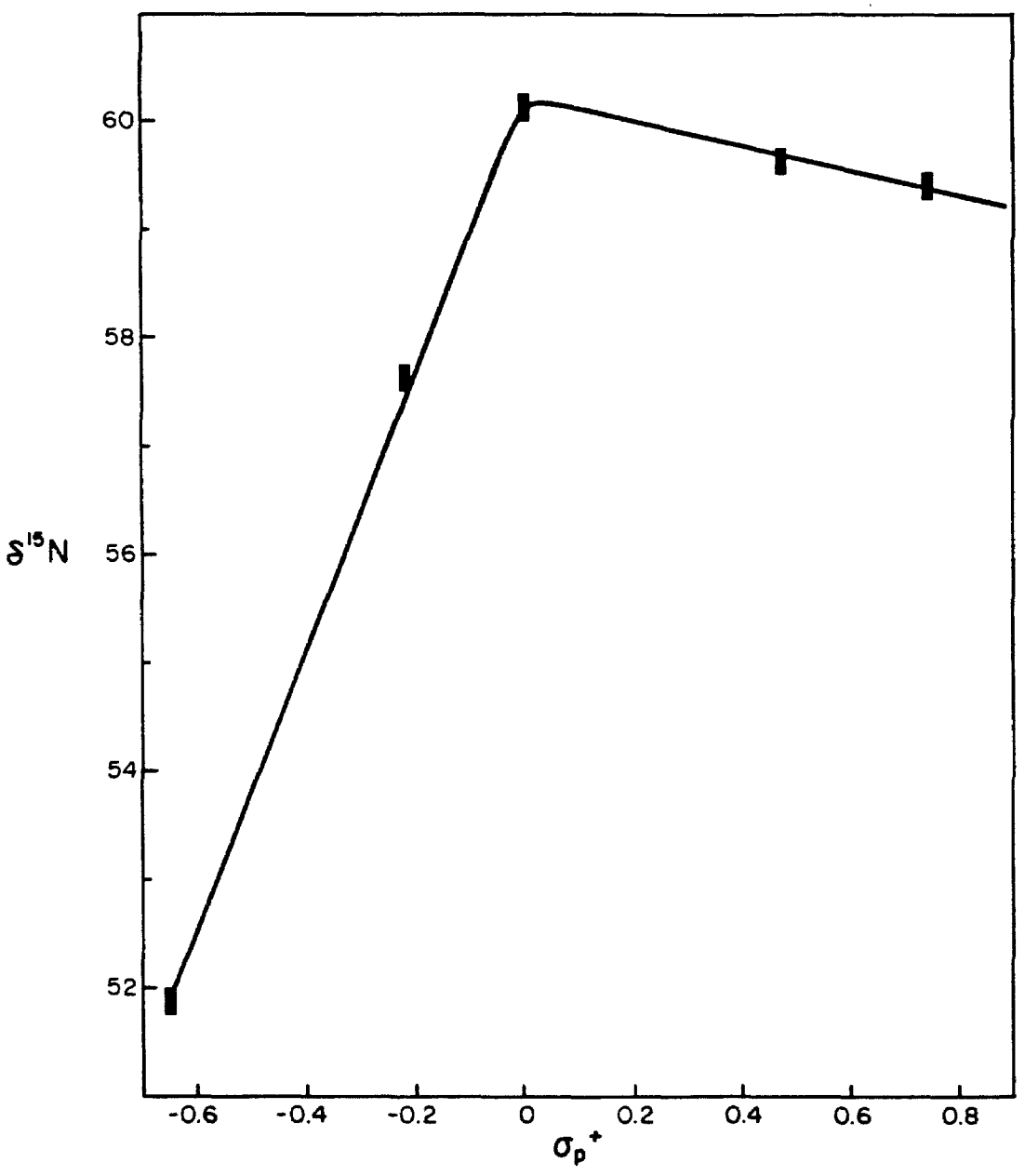


Figure 2. Plot of the N2 ^{15}N shifts of substituted aryldiazonium fluoborates against σ^+.

electron populations of gas-phase benzenediazonium ion (STO-3G) [35] and the X-ray structure of benzenediazonium chloride [6] and tribromide [37].

The arydiazonium salts with para groups more electron accepting than H seem to lie on a line of opposite slope relative to the electron-donating substituents. As the substituents become more electron withdrawing, the N2 resonances shift downfield - a trend which is not easily reconciled with the simple picture indicated by resonance structures Va-c. The curvature in Fig. 2 must be due to another factor increasing in importance as the substituent becomes more electron withdrawing. As the para substituent becomes more electron-withdrawing it is expected that resonance structures Vb and Vc will become less important and the positive charge on N2 will increase. Diamagnetic deshielding of N2 due to the increased positive charge might provide an explanation for the curvature in Fig. 2.

Crown Shifts

^{15}N and ^{13}C shifts induced by crown ether complexation have been determined for several para-substituted aryldiazanium salts in dimethylformamide. The crown shifts for II have also been measured in dichloromethane (Table IV). Addition of one equivalent of 18-crown-6 to the aryldiazonium salt solutions induces relatively small changes in the ^{13}C resonances. The para carbon (C4) shifts upfield and the C1 shifts downfield on complexation by 18-crown-6 for all salts examined. The crown induced ^{13}C changes for the n-butyl salt (II) in

TABLE IV. ^{13}C and ^{15}N Crown Shifts for Aryldiazonium Fluoborates [a]

Substituent	Solvent	δN1[b]	δN2[b]	δC1[b]	δC4[b]
O_2N-	DMF [c]	-	-	.5	- .5
H-	DMF [c]	-5.7	3.2	1.2	-1.1
(n-butyl)-	DMF [c]	-4.5	2.3	1.8	-1.8
(n-butyl)-	CH_2Cl_2	-5.8	2.0	3.9	-2.0
MeO-	DMF [c]	-4.5	1.5	2.6	-1.3

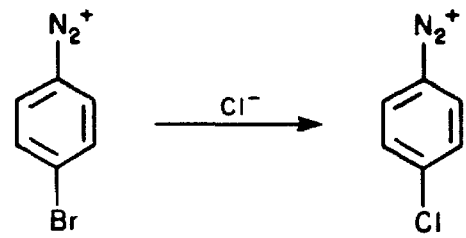
a Addition of one equivalent 18-crown-6.

b A positive crown shift indicates a downfield shift on complexation.

c Dimethylformamide.

dichloromethane are similar to those reported for the t-butyl salt in the same solvent [12].

These ^{13}C crown shifts are consistent with a decrease in the importance of diazo-like resonance structures (Vb,Vc) upon complexation. The diminished delocalization of the positive charge onto the ring by complexation with crown ether is also evident in the chemistry of complexed aryldiazonium salts. Gokel and coworkers [7] have shown that the nucleophilic aromatic substitution of p-bromobenzenediazonium fluoborate by chloride ion is stronly affected by complexation (3).



(3)

In fact, these workers find that reaction 3 is completely suppressed in the presence of ten equivalents of 18-crown-6. Both the reactivity and spectral changes on complexation point to reduced positive charge on the para carbon in the complexed diazonium cation.

The larger upfield shift of N1 on complexation also indicates a reduction of the diazo character in the complexed salt. The N2 resonance moves slightly downfield on complexation, a direction not consistent with increased diazonium character, unless, along with it, N2 experiences a strong diamagnetic deshielding due to the increased

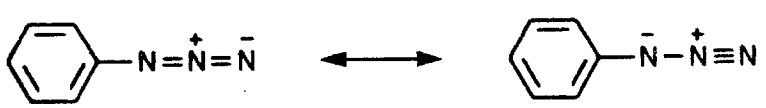
positive charge. Additional factors responsible for the downfield shift of the N2 resonance may be the displacement of solvent or counterion by the bulky crown ether.

Izatt and coworkers have studied the complexation of aryldiazonium cations with 18-crown-6 methanol by calorimetric titration [4]. The extent of complexation was found to be highest for the para-nitro substituent and an order of magnitude higher than for the para-methoxy. For this reason, until limiting shifts are obtained, using Table IV to determine trends in crown shift as a function of substituent is dangerous. However, it is notable that all of the C1 and some of the C4 crown shifts become larger as the para-substituent becomes more electron donating; the reverse of the expected equilibrium effect. This trend suggests that the more diazo-like the uncomplexed aryldiazonium cation, the larger the electronic perturbation, and hence shift, on complexation.

Crown Complexation of Related Systems

Several unsuccessful attempts to demonstrate crown complexation of related systems by ^{15}N NMR are described below.

Spectroscopic [37] and chemical studies [38] of phenyl azide indicate that the azido group has a resonance effect which is electron donating, in accord with an important contribution of resonance structure VIb.

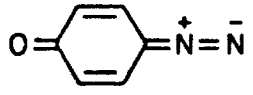


VIa VIb

It was thought that the diazonium-like terminus of phenyl azide might be complexed by 18-crown-6, and the electronic changes on complexation could be detected by ^{15}N NMR. The addition of one equivalent of 18-crown-6 to a 2.4 M solution of phenyl azide in chloroform did not result in any changes in the ^{15}N chemical shifts.

The possibility of crown complexation of p-toluenesulfonyl azide was also investigated because of its N-diazonium character. Addition of up to five equivalents of 18-crown-6 to a .1 M solution of ^{15}N-labeled p-toluenesulfonyl azide in dimethyl sulfoxide did not change the ^{15}N resonance positions.

No ^{15}N changes were observed after the addition of one equivalent of 18-crown-6 to a 1.4 M solution of diazoquinone tetrahydrate (VII) in dimethyl sulfoxide, also ruling out complexation.



VII

The addition of one equivalent of 18-crown-6 to a 1.9 M solution of benzonitrile in cyclohexane induced a 1.1 ppm upfield ^{15}N shift. The same change, however, was observed after addition of one equivalent of p-dioxane, indicating that the crown-benzonitrile interaction is not specific.

It appears that the compound must be a cation in order for complexation by 18-crown-6 to occur.

DISCUSSION

The ^{15}N and ^{13}C results are consistent with the Gokel-Cram [2] model of complexation, in which the N_2^+ group inserts into the hole of the crown ether. The crown complexation reduces delocalization of the positive charge by diazo-like resonance structures. Thus, the crown complexed salt is electronically more diazonium-like and less diazo-like than the uncomplexed form. The infrared studies of p-t-butylbenzenediazonium fluoborate in dichloromethane reported by Korzeniowski [12] support this interpretation. The approximately 40 cm^{-1} shift to higher NN stretching frequency upon complexation indicates a higher NN bond order in the complexed aryldiazonium salt. Infrared studies of solid 1:1 aryldiazonium salt/crown ether adducts also show such a frequency change relative to the solid uncomplexed salt [12,39]. Interestingly, the magnitude of the crown-induced infrared and N1 ^{15}N shifts are both comparable to the effects caused by a change in para substituent.

EXPERIMENTAL SECTION

Spectra

^{15}N NMR spectra were measured at 18.25 MHz with a Bruker WH-180 spectrometer using 15-25 mL samples in 25 mm sample tubes. Lock and reference signals were provided by a concentric 5-mm tube containing 1 M 95% $H^{15}NO_3$ in D_2O solution. All spectra were proton coupled and obtained at ambient probe temperature. The accumulation of 1000-4000 transients (20 μs pulse, 10S repetition rate) gave reasonable

signal/noise rations. ^{15}N solvent effects were determined for 1.2-1.6 M solutions of I and 1.9 M solutions of benzonitrile. Substituent effects for aryldiazonium fluoborates were obtained for .3-1.0 M solutions of the salt. Crown shifts were measured using .5-1.5 M solutions of aryldiazonium fluoborate.

^{13}C NMR spectra were taken at 45.28 MHz with a Bruker WH-180 spectrometer. A concentric 5-mm tube containing t-butyl alcohol in D_2O provided lock and reference signals. The reported shifts have been converted to the Me_4Si scale. The accumulation of 1000-2000 transients using 30 μs pulses gave satisfactory signal/noise ratios. Spectra of aryldiazonium salts were obtained for 1.4 M solutions at 14-15°C.

Materials

Commercially available spectrophotometric grade dichloromethane, nitromethane, acetonitrile, acetone, chloroform and cyclohexane were used in this study. The other solvents and benzonitrile used were commercial reagent grade. 18-crown-6 was purchased from Aldrich Chemical Co. and used without purification.

The aryldiazonium fluoborates were synthesized by standard techniques [40]. The p-(n-butyl)benzenediazonium and p-(t-butyl)-benzenediazonium floborates were purified by several recrystallizations from dichloromethane/diethyl ether and dichloromethane/pentane, respectively. The other salts were recrystallized from acetonitrile/ether.

A dichloromethane solution of p-(n-butyl)benzenediazonium chloride was prepared by treating the fluoborate in dichloromethane with one equivalent of tetramethylammonium chloride [41] The filtered solution was used immediately.

A mixture of 1-,2-, and 3- ^{15}N-labeled p-toluenesulfonyl azides was prepared as described previously [42]. Phenyl azide was synthesized using the method of Lindsay and Allen. [43] p-Diazoquinone was obtained from p-hydroxybenzenediazonium chloride [44] by the procedure of Puza and Doetschman [45].

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