yield 6.0 g (70%). Similarly, with benzaldehyde (5.3 g, 0.05 mol) instead of salicylaldehyde: **3** was formed: mp 365–370°; after sublimation, mp 388–390°, yield 2.8 g (33%).

2-(*p*-Nitrophenyl)acenaphthimidazole, 8.—Acenaphthenequinone (1, 9.1 g, 0.05 mol), *p*-nitrobenzaldehyde (7.56 g, 0.05 mol), 40 g of ammonium acetate, and 100 ml of acetic acid were heated at reflux 2 hr. The mixture was cooled to 25° and filtered to remove a solid which was washed with acetic acid, dried at 120° and 10 mm, and weighed 11.4 g. Extraction of the solid with 1000 ml of boiling ethanol dissolved 6.0 g. A second ethanol extraction dissolved in additional 2.5 g. The residue, 2.9 g, contained <1 g of **3** by thin layer chromatography, infrared analysis, and sublimation. The combined ethanol extracts were cooled to 5° and crystals formed. Filtration, washing with ethanol, and drying afforded **8**, 6.2 g, mp 300–305° (between 215 and 295° phase changes occur which have the appearance of partial melting and then resolidification). Recrystallization from ethanol and sublimation at 240° and 0.01 mm produced pure yellow-orange crystals of **8**, mp 310–312°. The infrared spectrum showed bands at 3000–2600 m (broad NH), 1587 ms, 1500 s (nitro, imidazole), 1470 s, 1330 s (nitro), 1310 s, 850 m (2 adjacent Ar H's), 812 m, 760 (acenaphthene H's) cm^{-1}.

Anal. Calcd for $C_{19}H_{11}N_3O_2$: C, 72.8; H, 3.54; N, 13.4. Found: C, 72.9; H, 3.45; N, 13.3.

A second crop of impure **8**, 1.0 g, was isolated from concentration of the ethanol extracts.

Oxidation of 3.—The procedure was similar to the one of Tsuge and Tashiro.[6] To a suspension of **3** (0.50 g, 1.45 mmol) in 15 ml of acetic acid was added 1.5 g of sodium dichromate. The mixture was heated at reflux (116°) for 1 hr. The dark red solution was poured into 50 ml of water, and the precipitate was filtered off and washed with water. The solid was triturated with 70 ml of 10% sodium carbonate solution for 1 hr. The solid that remained was collected on a filter, washed with water, and dried; wt 0.43 g; analysis indicated a mixture of 70% naphthalimide and 30% naphthalic anhydride. Acidification of the sodium carbonate solution afforded 0.04 g of crystals after drying, mp 294–302°. Anaysis indicated these to be 85% naphthalimide and 15% naphthalic anhydride. Ether extraction of the filtrate removed 0.07 g of a material which had an infrared and mass spectrum consistent with approximately one-third naphthalimide and two-thirds of the monoamide of naphthalic acid. Analyses of the three fractions were carried out by infrared and nmr. The spectra were compared with spectra of mixtures of naphthalimide and naphthalic anhydride of known composition. In addition, each fraction was sublimed to separate the more volatile anhydride from the imide. No melting point depressions were noted when each zone of the sublimate was mixed with the appropriate known compound. Mass spectra of the fractions were identical with mass spectra of the known compounds. The overall yields of the two major components were naphthalimide, 0.35 g (65%), and naphthalic anhydride, 0.13 g (24%).

Registry No.—Acenaphthenequinone, 82-86-0; ammonium acetate, 631-61-8; **3**, 24744-77-2; **8**, 17988-08-8.

A Novel Catalytic Salt Effect in Base-Initiated Aryne Reactions Conducted in Dimethylamine Solvent[1a]

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We have routinely carried out aryne reactions in dimethylamine[2] using bromo aromatic compounds with either sodamide or potassium amide as the base and a reaction time of 3 hr to prepare the corresponding N,N-dimethyl aromatic amines in high yields (90–93%). In addition, high yields of aromatic amines can be obtained using chloro aromatic compounds and potassium amide in dimethylamine. Recently, we have observed that the reaction of chlorobenzene and *o*- or *p*-chlorotoluene produces the corresponding aromatic amine in low yields (5–7%) if sodamide is used as the base. However, if these reactions are carried out in the presence of the sodium salts of certain nitriles (0.5 equiv per equiv of sodamide), high yields (67–78%) of the appropriate aromatic amines are obtained. In addition, a small amount (8–17%) of the corresponding

$$ArCl + NaNH_2 + NaCHRCN \xrightarrow{HN(CH_3)_2} ArN(CH_3)_2 + ArCHRCN$$

arylated nitriles is produced. Table I summarizes the aforementioned results.

In addition the yields of N,N-dimethylaniline obtained from the action of sodamide on chlorobenzene are increased from 5 (no salt present) to 28, 56, and 56% by the addition of 0.8 equiv/equiv of sodamide of the inorganic salts, sodium nitrite, sodium thiocyanate, and potassium thiocyanate, respectively. Similarly, the yields of N,N-dimethyl-*o*- and -*m*-toluidines obtained from the action of sodamide on *o*-chlorotoluene are increased from 5 to 50, 80, and 80% by the addition of 0.8 equiv of sodium nitrite, sodium thiocyanate, and potassium thiocyanate, respectively. The isomer ratios of the N,N-dimethyltoluidines are in all cases 53:47, *ortho*:*meta*, respectively. In contrast, no increase in yields is observed by the addition of the salts KCl, KBr, NaCl, NaBr, Na_2SO_4, $NaNO_3$, KNO_3, or KI.

The specific action of only certain salts in increasing the conversion of chloro aromatics argues against a general salt effect. In addition, it appears that the anion portion of the salt is responsible for the catalytic behavior. Interestingly, only those salts which are linear and in which the negative charge is resonance stabilized appear to be effective catalysts. See, for example

$$^-CH_2—C\equiv N \longleftrightarrow CH_2=C=N^-$$

$$^-S—C\equiv N \longleftrightarrow S=C=N^-$$

Since the rate-determining step of the aryne reaction[3] is the abstraction of a hydrogen atom by a strong base, it appears that the salts are increasing the base strengths of sodamide in liquid dimethylamine. This action could either be the result of the salts (1) increasing the concentration of sodamide in dimethylamine, or (2) effecting a change in the aggregate populations which most likely exist in dimethylamine. Unfortunately, little is known concerning (1) the solubility of sodamide in dimethylamine, (2) the effect of salts on the solubility of sodamide in dimethylamine, and, most importantly, (3) the form in which sodamide exists in dimethylamine. We currently are investigating the mechanistic aspects of these unusual catalytic effects.

(1) (a) Supported in part by R. A. Welch Grant N-118, Houston, Texas; (b) Robert A. Welch Predoctoral Fellows.

(2) Reactions of this general type were first developed for synthetic purposes by J. F. Bunnett and T. K. Brotherton, *J. Org. Chem.*, **22**, 832 (1957).

(3) J. D. Roberts, D. A. Semenow, H. E. Semenow, and L. A. Carlsmith, *J. Amer. Chem. Soc.*, **78**, 601 (1956).

TABLE I

REACTION OF HALO AROMATIC COMPOUNDS WITH ALKALI AMIDES IN DIMETHYLAMINE

Halo aromatic, GC_6H_4X			Salt, NaCHRCN	N,N-Dimethylarylamines			Arylated salt		
					Isomer ratio[a]			Isomer ratio[a]	
G	X	Base	R	Yield, %	o:m	m:p	Yield, %	o:m	m:p
H	Br	$NaNH_2$		91					
H	Br	KNH_2		93					
H	Cl	KNH_2		87					
H	Cl	$NaNH_2$		5					
H	Cl	$NaNH_2$	H	78			11		
H	Cl	$NaNH_2$	C_6H_5	68			8		
o-CH_3	Cl	KNH_2		90	53:47				
o-CH_3	Cl	$NaNH_2$		5	53:47				
o-CH_3	Cl	$NaNH_2$	H	62	53:47		17	50:50	
o-CH_3	Cl	$NaNH_2$	C_6H_5	67	53:47		14	50:50	
p-CH_3	Cl	KNH_2		90		50:50			
p-CH_3	Cl	$NaNH_2$	H	64		50:50	18		50:50

[a] Isomer ratios were determined by vpc analysis.

Experimental Section[4]

Chemicals.—All starting halo aromatic compounds and potassium were obtained from J. T. Baker Chemical Co. and were of the highest purity grade available. Sodamide was obtained from Fisher Chemical Co. and was used as received. Anhydrous dimethylamine was obtained from Matheson Co. and was distilled directly into the reaction flask through an anhydrous potassium hydroxide filled drying tube. All inorganic salts were thoroughly dried under vacuum at 110° for 24 hr and then stored in a drybox until use. All weighing procedures of the salts were also carried out in the drybox.

General Procedure for the Aryne Reaction.—In a typical experiment, the organic salt was prepared by adding 0.2 mol of the approximate nitrile to a stirred suspension of 0.4 mol of sodamide or potassium amide (prepared by the action of 0.4 g-atom of potassium in 200 ml of ammonia in the presence of 0.01 g of ferric nitrate, followed by removal of ammonia) in 500 ml of anhydrous dimethylamine. The inorganic salt (0.05 mol) was added directly to a stirred suspension of the base in 500 ml of anhydrous dimethylamine. After 30 min, the appropriate halo aromatic compound was added over a period of 5 min and the resulting mixture was allowed to stand for an additional 3 hr. At this time, the mixture was quenched by the addition of 0.45 mol of ammonium chloride and the solvent was removed by heating with a steam bath. The residue was washed out of the flask first with 150 ml of water and then with 100 ml of ether. The combined mixture was filtered, acidified with 50 ml of 6 *N* hydrochloric acid and was extracted with several portions of ether to remove the arylated acetonitrile and starting halo-aromatic compound. The acidic aqueous layer was made basic by the addition of sodium hydroxide (pH 14) and then was extracted with several portions of ether in order to remove the arylated amines. The combined acidic and basic ether extracts were dried (sodium sulfate), concentrated, and distilled in order to determine the percentage yields of each product.

Authentic Compounds.—N,N-Dimethylaniline was purchased from Aldrich Chemical Co. N,N-Dimethyl-*o*-toluidine, bp 98–99° (17 mm) [lit.[5] bp 98.5–99° (17 mm)], and N,N-dimethyl-*m*-toluidine, bp 207–208° (atm) [lit.[5] bp 206–207° (atm)], were prepared by the method of Hünig.[5] Phenylacetonitrile was purchased from Eastman Kodak Co. Diphenylacetonitrile, mp 73–74° (lit.[6] mp 73.5–74.5), was prepared by the method of Leake,[7] whereas *o*-methylphenylacetonitrile, bp 244° (atm) [lit.[8] bp 244° (atm)], *m*-methylphenylacetonitrile, bp 116° (8.5 mm) [lit.[8] bp 133° (15 mm)], and *p*-methylphenylacetonitrile, bp 122° (13 mm) [lit.[9] bp 122 (13 mm)], were prepared by the method of Titley.[8]

Registry No.—Bromobenzene, 108-86-1; chlorobenzene, 108-90-7; *o*-chlorotoluene, 95-49-8; *p*-chlorotoluene, 106-43-4; $NaNH_2$, 24781-98-4; KNH_2, 24781-99-5; acetonitrile (sodium salt), 14904-37-1; phenylacetonitrile (sodium salt), 14904-38-2.

(4) All melting points are uncorrected. The quantitative determinations were performed on a MicroTek Instrument Model GC 1600 using helium as the carrier gas at a flow rate of 45 ml/min and inlet and detector temperatures at 300°. A 5 ft × 1/8 in. i.d. column packed with 3% SE-30 (silicone rubber) on Chromosorb W, acid washed, mesh 80–100, was used to analyze the nitriles whereas the amines were analyzed using a 10 ft × 1/8 in. i.d. column packed with 5% Carbowax 20M (polyethylene oxide) on Chromosorb W, acid washed, 60–80 mesh. The peak areas were measured by a Ball-Disc integrator, an integral part of the Sargent recorder Model SR. The chromatographic bands were identified by comparing their retention times with those of authentic samples. Percentages of each compound were calculated from the areas of the bands. These areas were assumed to be equal to the peak height times the width at one-half peak height. Molar response ratios were determined and the observed areas were corrected as necessary.

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Quinazolines and 1,4-Benzodiazepines. XLV.[1a] 1,4-Benzodiazepines from 4-Isoquinolones

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In connection with our interest in examining new possibilities for the synthesis of 1,4-benzodiazepine derivatives,[1b] we have examined the ring expansion of some substituted 2,3-dihydro-4(1H)-isoquinolones.

In our initial experiments (Scheme I) we prepared the oxime **2** from the known isoquinolone **1**[2] and examined the products obtained by treating this with polyphosphoric acid. In addition to the expected Beckmann rearrangement product, the benzodiazepinone **4**, we also obtained the isoquinolinium salt **3**. In fact, **3** was the major product found in the reaction mixture and was obviously the result of a Schroeter type of dehydration reaction.[3] A possible mechanism for the

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