boiling isomer is the *trans* compound. The chemical shifts of both methine protons in the *cis* isomer are found at lower field.

Registry No.—Hydrogen chloride, 7647-01-0; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *erythro*-3-chloro-2-methyl-1-butanol, 21430-05-7; 3,5-dinitrobenzoate ester of *erythro*-3-chloro-2-methyl-1-butanol, 21430-06-8; *threo*-3-chloro-2-methyl-1-butanol, 21430-07-9; 3,5-dinitrobenzoate ester of *threo*-3-chloro-2-methyl-1-butanol, 21430-08-0; *cis*-4-chloro-3-methyltetrahydropyran, 18755-76-5; *trans*-4-chloro-3-methyltetrahydropyran, 18755-77-6.

Acknowledgments.—We wish to thank Mrs. Joy Buell for recording the nmr spectra, Mr. F. L. Tilley for carrying out the double-resonance experiments, and Mr. C. G. Long for carrying out the preparative gas chromatographic separations.

Substituent Effects on the Reactivity of Arynes. Product Distributions as an Index of Relative Reactivities of Arynes in Methylamine and Dimethylamine Solvents[1a]

EDWARD R. BIEHL, EDWARD NIEH,[1b] AND K. C. HSU[1b]

Department of Chemistry, Southern Methodist University, Dallas, Texas 75222

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The competition between the anion of acetonitrile and methyl- or dimethylamine for various substituted arynes has been studied. The product distribution, per cent amine/per cent nitrile, was found to increase in all cases as the substituent was varied along a series, H, CH_3, OCH_3, Cl, and F, with a more marked increase in the product distribution being observed for 3-arynes than for 4-arynes. In addition, a linear free-energy relationship has been found between the log (% amine/% nitrile)$_G$/ (% amine/% nitrile)$_H$, where the subscripts G and H represent the substituted and unsubstituted benzyne intermediates, respectively, and the absolute value of the polar substituent constant, σ'. Therefore, it is concluded that both +I and −I substituents destabilize arynes by inductively polarizing the "triple bond" of benzyne.

There is ample evidence that the highly reactive aryne intermediates do possess some degree of selectivity.[2] For example, arylation of anions of active hydrogen compounds by phenyl halides occurs in high yields even though the reactions are carried out in the presence of amide ion and a large excess of the nucleophilic solvent, ammonia.[3] However, only one study on substituent effects on aryne selectivities has been reported.[4] In that investigation, the selectivities of 3-substituted benzynes were determined by studying the relative rates of addition of phenyllithium *vs.* lithium piperidide to the arynes in ether. The results indicated that −I (electron withdrawing by induction) substituents [OCH_3, $N(CH_3)_2$, and CF_3], by facilitating nucleophilic addition, decreased the selectivity of the aryne intermediate. By contrast, the +I (electron releasing by induction) substituent (CH_3), by retarding nucleophilic addition, increased the selectivity of the aryne intermediate. Experimental data concerning effects of 4 substituents on aryne selectivities were not reported. Recently, Zoltewicz and Bunnett[5] have obtained indirect evidence that the 4-methyl substituent may actually decrease the stability of the aryne intermediate generated not in ether but in liquid ammonia by the action of potassium amide on 4-chlorotoluene-3-*d*.

During the course of our investigation of the extension of the general aryne–carbanion arylation reaction, initiated by sodium amide in liquid ammonia, we have noted that the yields of arylated carbanions gradually decreased with a gradual increase in the yields of arylated amines as the substituent of the substituted phenyl halide was varied along the series H, CH_3, OCH_3, and Cl.[6] It has been demonstrated[7] that the predominant amine nucleophile in sodium amide initiated aryne reactions is the solvent molecule, ammonia. These results, therefore, indicate that the gradual increase in the amine yield with the above substituent variation was due to a gradual increase in the reactivity of the aryne intermediate toward the less reactive but more abundant ammonia molecule as compared with the carbanions.

Accordingly, the product distribution should serve as a measure of the influence of substituents on aryne reactivity. Therefore, a systematic study of the product distributions obtained from competition between carbanions and ammonia for various arynes was initiated.

Quantitative determinations of product distributions obtained from aryne reactions carried out in liquid ammonia were hampered by the formation of polyarylated amine and acetonitrile compounds. More recently, Hsu[8] has observed that the competition reactions between acetonitrile anion and the solvent, methyl- or dimethylamine, for various arynes (generated from the corresponding haloaromatic compound and sodium amide) yielded predominantly monoarylated products (80–90%) with only small amounts (10–20%) of polyarylated product being formed. Quantitative material balances, however, were not attempted in that study.

This paper reports on the study of the quantitative determinations of the various product distributions

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[1] (a) Supported in part by Grant No. N-118 from the Robert A. Welch Foundation, Houston, Texas; (b) Robert A. Welch Predoctoral Fellows.

[2] R. W. Hoffman, "Dehydrobenzene and Cycloalkynes," Academic Press, New York, N. Y., 1967, pp 246–250.

[3] For reviews, see J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); H. Heaney, *Chem. Rev.*, **62**, 81 (1962).

[4] R. Huisgen, W. Mack, and L. Mobius, *Tetrahedron*, **9**, 29 (1959); R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

[5] J. A. Zoltewicz and J. F. Bunnett, *J. Amer. Chem. Soc.*, **87**, 2640 (1965).

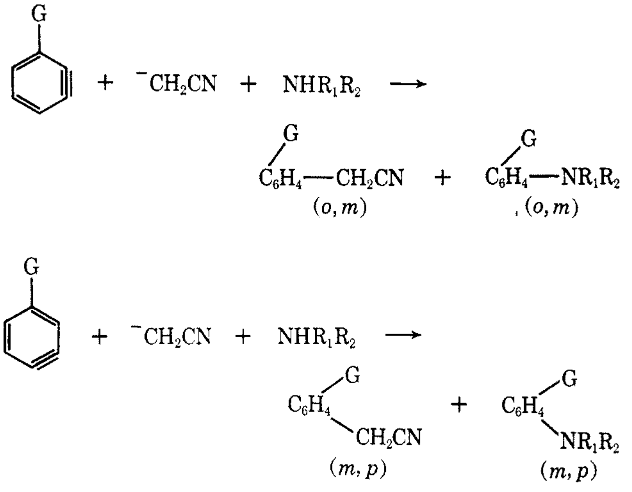
[6] Unpublished results.

[7] E. R. Biehl, E. Nieh, H. Li, and C. Hong, *J. Org. Chem.*, **34**, 500 (1969).

[8] K. C. Hsu, Master's Thesis, Southern Methodist University, 1967.

obtained from the competition between the anion of acetonitrile and methyl- or dimethylamine for 3- and 4-arynes possessing the substituents, H, CH_3, OCH_3, Cl, and F (Scheme I). Yields and isomer ratios were determined by gas–liquid chromatographic analysis.

Scheme I



G = H, CH_3, OCH_3, Cl, and F
$R_1 = R_2 = CH_3$
$R_1 = H$; $R_2 = CH_3$

Experimental Section[9]

Starting Materials.—The *o*- and *p*-bromotoluenes, *o*- and *p*-dichlorobenzenes, bromobenzene, and acetonitrile were obtained from J. T. Baker Chemical Co.; the *o*- and *p*-bromoanisoles and *o*- and *p*-bromobenzonitriles were obtained from Eastman Kodak Co.; the *o*- and *p*-bromofluorobenzenes were obtained from Pierce Chemical Co. These materials were of highest purity grade available and were distilled or recrystallized at least once before using. Sodium amide was obtained from Fisher Chemical Co. and was used as received. Anhydrous methyl- and dimethylamines were obtained from Matheson Co. and were distilled directly into the reaction flask through an anhydrous potassium hydroxide filled drying tube.

General Procedure for the Aryne Reaction.—The reactions were performed in a 1-l. three-necked flask equipped with stirrer, Dry Ice condenser, and drying tube, using mole ratios of 8:5:1, 4:2:1, and 5:3:1 of sodium amide/acetonitrile/haloaromatic compound, respectively, in 500 ml of anhydrous methyl- or dimethylamine. In a typical experiment, acetonitrile was added over a period of 5 min to a stirred suspension of sodium amide and amine solvent and the mixture was stirred for an additional 15 min to ensure complete anion formation. After the addition of the appropriate haloaromatic compound, the mixture was stirred for an additional 3 hr.[10] After this time, the reaction mixture was quenched (0.1 mol excess 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 100 ml of ether. The combined mixture was filtered, acidified with 50 ml of 6 *N* hydrochloric acid, and extracted with several portions of ether to remove the arylated acetonitriles. The acidic aqueous layer was made basic by the addition of sodium carbonate until carbon dioxide evolution ceased, followed by the addition of 5 g of sodium hydroxide, and then was extracted with several portions of ether to remove the arylated amines. The combined acidic and basic ether extracts were dried (sodium sulfate), concentrated, and analyzed by gas chromatography.

General Procedure for Quantitative Analysis of Reaction Mixture.—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°. The peak areas were measured by a ball-disk integrator, an integral part of the Sargent recorder, Model SR. A 5 ft × 0.125 in. i.d. column was 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 × 0.125 in. i.d. column packed with 5% Carbowax 20M (polyethylene oxide) on Chromosorb W, acid washed, 60–80 mesh. The direct comparison method[11] was used to determine the per cent yields.

Products. Authentic Samples. A. Arylacetonitriles.—Phenylacetonitrile (Eastman Kodak Co.), *m*- and *p*-chlorophenylacetonitriles (Aldrich Chemical Co.), *m*- and *p*-fluoroacetonitriles (Pierce Chemical Co.), and *p*-methoxyphenylacetonitrile (Aldrich Chemical Co.) were obtained as commercial samples and were distilled until chromatographically pure. The other nitriles, $ArCH_2CN$, were synthesized from the corresponding toluenes, $ArCH_3$, *via* their bromides, $ArCH_2Br$, in a manner similar to that described by Ipatieff, *et al.*,[12] with the exception that reaction times of 4 hr for both the NBS brominations and aryl–bromide–sodium cyanide reactions were used. Boiling points of the synthesized nitriles, *m*-methoxy-,[13] *o*-methyl-,[14] *m*-methyl-,[14] and *p*-methylphenylacetonitriles[15] were in good agreement with literature values.

B. **N-Methylarylamines.**—These compounds were prepared by the acid hydrolyses (refluxing 6 hr with 25% sulfuric acid) of the corresponding N-methylacetanilides. N-Methylacetanilides were prepared by the methylation of the appropriate N-sodio derivatives in a manner similar to that described by Millson and Robinson[16] with the exception that sodium was used in lieu of sodium amide for the preparation of the N-sodio derivatives. Boiling points of the synthesized amines, N-methyl-*o*-,[17] N-methyl-*m*-,[16] and N-methyl-*p*-anisidenes,[18] *o*-chloro-,[19] *m*-chloro-,[19] and *p*-chloro-N-methylanilines,[19] *m*-fluoro-[20] and *p*-fluoro-N-methylanilines,[20] and N-methyl-*o*-,[21] N-methyl-*m*-,[22] and N-methyl-*p*-toluidines[22] were in good agreement with literature values.

C. **N,N-Dimethylarylamines.**—These compounds were prepared in a similar manner to that described by Hünig.[23] Boiling points of the synthesized amines, N,N-dimethylaniline,[24] N,N-dimethyl-*o*-,[22] N,N-dimethyl-*m*-,[22] and N,N-dimethyl-*p*-anisidines,[25] N,N-dimethyl-*o*-,[26] N,N-dimethyl-*m*-,[27] and N,N-dimethyl-*p*-chloroanilines,[28] N,N-dimethyl-*m*-[28] and N,N-dimethyl-*p*-fluoroanilines,[29] and N,N-dimethyl-*o*-,[23] N,N-dimethyl-*m*-,[23] and N,N-dimethyl-*p*-toluidines[23] were in good agreement with literature values.

Results and Discussion

Dimethylamine System.—The competition between the anion of acetonitrile and dimethylamine for the aryne intermediate yielding arylated acetonitrile and amine products was first studied since polyarylation of dimethylamine is not possible. The results are listed in Table I. The arylated amine products were found

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(9) The melting points were taken on a Fisher-Johns block and are uncorrected.

(10) Previous experiments showed that 3 hr was sufficient to convert quantitatively haloaromatic compounds into products.

(11) A. R. Littlewood, "Gas Chromatography, Principle, Technique, and Application," Academic Press, New York, N. Y., 1962, p 215.

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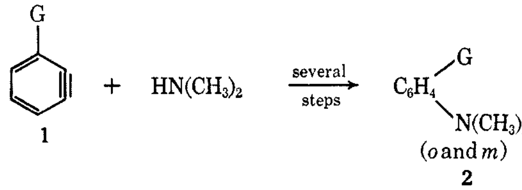
TABLE I

REACTION OF ARYL HALIDES WITH ACETONITRILE AND SODIUM AMIDE IN DIMETHYLAMINE

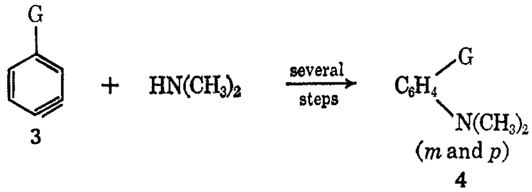
	G–C₆H₄–X		Arylacetonitrile			N,N-Dimethylarylamine			
			Yield,[a]	Isomer ratio[b]		Yield,	Isomer ratio		Amine (yield, %)/ nitrile (yield, %)
Run	G	X	%	*ortho/meta*	*meta/para*	%	*ortho/meta*	*meta/para*	
1	H	Br	38.0			62.0			1.63
2	o-CH_3	Br	32.2	50:50		67.8	53:47		2.10
3	o-OCH_3	Br	19.0	0:100		81.0	0:100		4.26
4	o-Cl	Cl	10.0	2:98		90.0[c]	0:100		9.00
5	o-F	Br	9.0	0:100		91.0	0:100		10.11
6	o-CF_3	Br	*d*			*d*			
7	p-CH_3	Br	35.7		50:50	64.3		50:50	1.80
8	p-OCH_3	Br	24.4		50:50	75.6		50:50	3.10
9	p-Cl	Cl	19.0		50:50	81.0[c]		37:63	4.26
10	p-F	Br	18.0		50:50	82.0		30:70	4.55
11	p-CF_3	Br	*d*			*d*			

[a] Di- and triarylated acetonitrile included. [b] Only for monoarylated acetonitriles. [c] Includes *ca.* 70% yields of N,N,N,N-tetramethylphenylenediamine isomers. [d] Value not attainable owing to excessive tar formation.

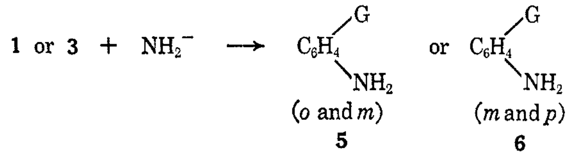
in all cases to be either the corresponding *ortho*- and *meta*-substituted N,N-dimethylarylamines, **2**, formed by addition of dimethylamine to the appropriate 3-arynes, **1** (eq 1), or the corresponding *meta*- and *para*-substituted N,N-dimethylamine, **4**, formed by dimethylamine addition to the appropriate 4-arynes, **3** (eq 2). In no case were the primary arylamines, **5** and **6**, observed, indicating that no amide addition occurred. Also, the low solubility of sodium dimethylamide in dimethylamine coupled with the low acidity of dimethylamine toward amide ion argues against appreciable dimethylamide ion addition (eq 3). Although polyarylation of dimethylamine is not possible, polyarylation of acetonitrile as well as monoarylation is not only possible but was indeed observed. For example, the reaction of chlorobenzene with acetonitrile yielded phenyl-, diphenyl-, and triphenylacetonitrile. Similar results were observed for the other aryl halides. Owing to the rather large number of possible di- and triarylated acetonitrile isomers, no attempt was made to determine the percentage yields of the arylated nitrile. However, a quantitative conversion of the aryl halides into products was achieved by using a mole ratio of 1 equiv of aryl halide/5 equiv of acetonitrile/8 equiv of sodium amide and a reaction time of 3 hr. Since the yields of the monoarylated amines could be determined quite accurately by means of vpc analysis, the total per cent yields of the mono- and polyarylated nitrile were calculated by the equation 100% − % yield of amines.



(1)



(2)



$$1 \text{ or } 3 + NH_2^- \longrightarrow \underset{\substack{(o \text{ and } m)\\ \mathbf{5}}}{C_6H_4\!\begin{smallmatrix}G\\NH_2\end{smallmatrix}} \text{ or } \underset{\substack{(m \text{ and } p)\\ \mathbf{6}}}{C_6H_4\!\begin{smallmatrix}G\\NH_2\end{smallmatrix}} \qquad (3)$$

Interestingly, a good yield (70%) of N,N,N,N-tetramethyl-*m*-phenylenediamine, **7**, was formed in the reaction of *o*-dichlorobenzene with sodium amide in dimethylamine. Similarly, an isomeric mixture (70% yield) of N,N,N,N-tetramethyl-*m*- and -*p*-phenylenediamine (**7** and **8**, respectively) (60:40 *meta/para*, respectively) was isolated from the reaction of *p*-dichlorobenzene under the same conditions as above. The formation of **7** is probably the result of a "double benzyne" reaction of *o*-dichlorobenzene which is illustrated in Scheme II. Treatment of *o*-dichlorobenzene with sodium amide yields 3-chlorobenzyne, **9**, which upon addition of dimethylamine yields the dipolar intermediate, **10**. A prototropic shift in **10** affords *m*-chloro-N,N-dimethylaniline, **11**. Although **11** could have formed either 3- or 4-dimethylaminoaryne by treatment with sodium amide, only the 3-aryne, **12**, is formed owing to the greater acidity of the benzenoid hydrogen atom located *ortho* to the dimethylamine group compared with that *para* to the dimethylamine group. Addition of dimethylamines to the *meta* position of **12** leads ultimately to **7**. A similar mechanism for the reaction of *p*-chlorobenzene can be proposed with the exception that addition of dimethylamine occurs at both positions of 4-chlorobenzyne, **13**,

SCHEME II

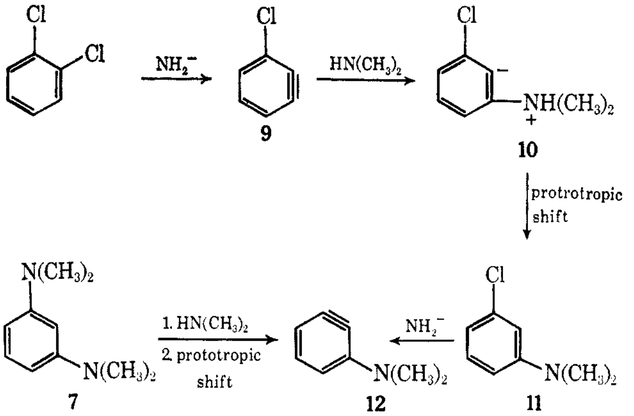


TABLE II

REACTION OF ARYL HALIDES (1 EQUIV) WITH ACETONITRILE (3 EQUIV) AND SODIUM AMIDE (5 EQUIV) IN METHYLAMINE

	G-C_6H_4-X		Arylated Acetonitriles			N-Methylanilines			Amine (yield, %[a])/ nitrile (yield, %)
			Yield,[a]	Isomer ratio[b]		Yield,[a]	Isomer ratio[b]		
Run	G	X	%	*ortho/meta*	*meta/para*	%	*ortho/meta*	*meta/para*	
1	H	Br	36.8			47.6			1.3
2	*o*-CH_3	Br	33.3	50:50		49.9	65:35		1.5
3	*o*-OCH_3	Br	12.6	2:98		73.0	2:98		5.8
4	*o*-F	Br	5.1	2:98		77.8	2:98		15.3
5	*o*-CF_3	Br	*c*			*c*			
6	*o*-Cl	Cl	*d*			*d*			
7	*p*-CH_3	Br	37.9		50:50	52.5		50:50	1.4
8	*p*-OCH_3	Br	32.4		50:50	56.3		50:50	1.7
9	*p*-F	Br	23.8		50:50	65.5		32.68	2.8
10	*p*-CF_3	Br	*c*			*c*			
11	*p*-Cl	Cl	*d*			*d*			

[a] Based only upon monoarylated products on the assumption that diarylated products were formed in same ratio as that of monoarylated products. [b] Only for monoarylated products. [c] Value not obtained owing to extensive tar formation. [d] Value not obtained owing to inability to achieve complete separation of chloro-N-methylanilines from acidic compounds.

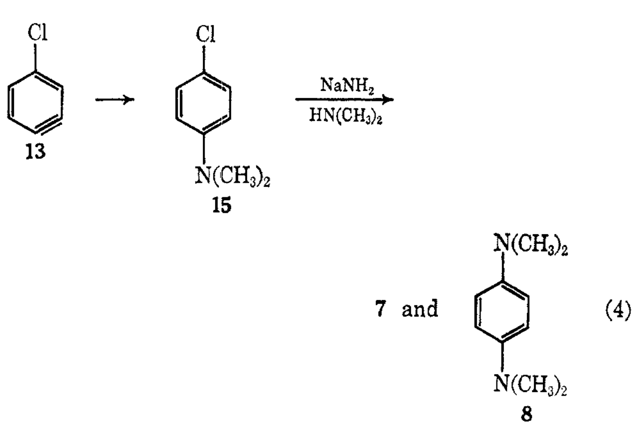
TABLE III

REACTIVITY FACTORS AND POLAR SUBSTITUENT CONSTANTS FOR 3- AND 4-SUBSTITUTED ARYNES

Substituent	Solvent	R.F.	σ'	σ_{meta}	σ_{para}
3-CH_3	Dimethylamine	0.111	−0.05	−0.069	−0.170
3-OCH_3		0.417	+0.23	+0.115	−0.260
3-Cl		0.742	+0.47	+0.37	+0.24
3-F		0.792	+0.50	+0.34	+0.06
4-CH_3		0.0414	−0.05	−0.069	−0.170
4-OCH_3		0.279	+0.23	+0.115	−0.260
4-Cl		0.417	+0.47	+0.37	+0.24
4-F		0.447	+0.50	+0.34	+0.06
3-CH_3	Methylamine	0.061	*a*	*a*	*a*
3-OCH_3		0.650	*a*	*a*	*a*
3-F		1.070	*a*	*a*	*a*
4-CH_3		0.033	*a*	*a*	*a*
4-OCH_3		0.117	*a*	*a*	*a*
4-F		0.332	*a*	*a*	*a*

[a] Same value as above.

to yield both *m*- and *p*-chloro-N,N-dimethylanilines, **15**, which upon further treatment with sodium amide and dimethylamine are converted into **7** and **8** (eq 4).



The ratios of the per cent yields of the arylated amines to arylated nitriles listed in Table I show that both −I substituents (OCH_3, Cl, and F) and the +I substituent (CH_3) render the corresponding 3- and 4-arynes more vulnerable to amine attack than benzyne itself. Since the higher degree of solvent attack is most likely a consequence of the higher reactivity of the arynes compared with benzyne, these results indicate that both +I and −I substituents destabilize arynes. Moreover, the product ratios increase continually from 1.6 to 9.0 (3-aryne systems) and from 1.6 to 6.8 (4-aryne systems) as the substituent is varied along the series H, CH_3, OCH_3, Cl, and F which is in the order of increasing σ' (inductive) substituent constants. This indicates that the substituents apparently destabilize arynes by inductively polarizing the "triple bond" of the arynes.

Methylamine Systems

The results of the competition between the anion of acetonitrile and methylamine are listed in Table II. The total yield of monoarylated nitriles and amines ranged from 82.0 (run 4) to 90.4% (run 6), indicating that relatively little polyarylation occurred. Qualitative infrared analysis indicated that both polyarylated nitriles and amines were formed in approximately the same ratio as the monoarylated products. Therefore, the ratios of the amine to nitrile per cent yields were calculated on the basis of the per cent yields of the monoarylated products.

As was previously observed in the dimethylamine system, the per cent yields of amine in the methylamine system were found to increase as the substituent of both 3- and 4-arynes was varied along the series (of increasing inductive effect) H, CH_3, OCH_3, and F,

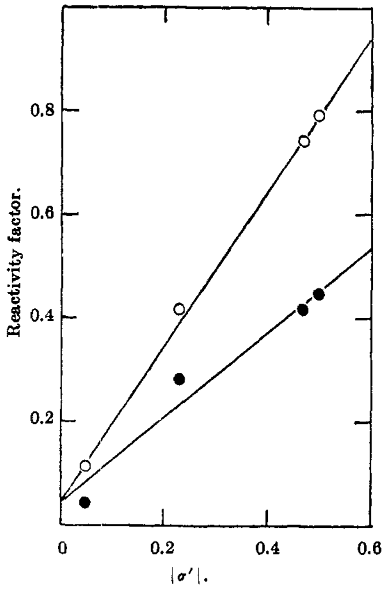


Figure 1.—Plots of reactivity factor *vs.* |σ'| in dimethylamine where ○ represents 3-arynes and ● represents 4-arynes.

indicating that both +I and −I destabilize arynes.[30] Furthermore, the product ratio ranged from 1.3 to 15.3 in 3-aryne systems whereas in 4-aryne systems, the ratio varied from 1.3 to 2.8. These results are, again, consistent with the argument that the mode by which substituents destabilize arynes is inductive in nature.

Linear Free-Energy Relationships.—Many linear free-energy relationships have been developed to correlate kinetic and equilibrium data. One of the most important of these is the Hammett relationship[31] which has the general form

$$\log \frac{k}{k_0} = \sigma\rho$$

where k_0 is the rate or equilibrium constant for the reaction of the unsubstituted compound and k is the rate or equilibrium constant for the corresponding substituted compound. The two parameters, σ and ρ, yield information concerning the electrical nature of the substituents and the electron demand of the reaction.

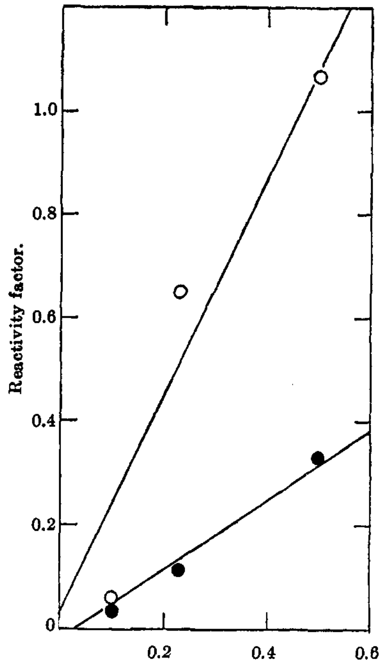


Figure 2.—Plots of reactivity factor *vs.*| σ'| in methylamine where ○ represents 3-arynes and ● represents 4-arynes.

It can be shown,[32] theoretically, that a free-energy relationship also exists between the polar substituent constants and the reactivity factor (R.F.) defined as

$$\text{R.F.} = \log (\%\ \text{amines}/\%\ \text{nitriles})_G/(\%\ \text{amines}/\%\ \text{nitriles})_H$$

where (% amine/% nitrile)$_G$ is the product ratio for a substituted aryne and (% amine/% nitrile)$_H$ is the product ratio for the unsubstituted aryne, benzyne. Table III lists the reactivity factors and the corresponding polar substituent constants for the corresponding substituted arynes. As expected, only |σ'| values yield a straight line when plotted against the various R.F. for 3- or 4-arynes in dimethylamine (Figure 1) and methylamine (Figure 2), respectively.

Interestingly, this experimental method affords a means of determining substituent effects on the reactivity of arynes even though in usual cases a statistical distribution of both amine and nitrile products were obtained.

Registry No.—Methylamine, 74-89-5; dimethylamine, 124-40-3; anion of acetonitrile, 21438-99-3.

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(30) Results for the chlorine substituent could not be obtained owing to the low basicity of *o*- and *p*-chloro-N-methylaniline. Complete separation of these bases from the nonbasic components could not be achieved even using 20% hydrochloric acid solutions.

(31) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 184.

(32) E. Nieh, M.S. Thesis, Southern Methodist University, 1968, p 11.