although catalyst frequency numbers were still low.

Analysis of fresh ruthenium sulfide by ESCA showed ruthenium to be in the 4+ valency state, corresponding to RuS_2. The spent catalyst was divalent (2+), corresponding to RuS. Treatment of the latter with sodium sulfide solution restored its 4+ valence. Metallic ruthenium was never detected by ESCA in the hydrogenation work over ruthenium sulfides. This indicates that hydrogenations in the sulfide system are mechanistically different from those employing metallic ruthenium.

Finally, in hydrogenation of *m*-dinitrobenzene over cobalt polysulfide or ruthenium sulfide, both catalysts gave *m*-phenylenediamine exclusively (100 °C, 1000 psig H_2). This indicates that hydrogenations over transition metal sulfides in a neutral medium are mechanistically different from the conventional alkali metal sulfide reductions in basic medium, where only *m*-nitroaniline is formed.[18]

Experimental Section

All hydrogenations were carried out in a Parr low-pressure shaker (500-mL), or in 1-L, 1-gal, or 5-gal, 316-stainless steel, magnetically stirred autoclaves (Autoclave Engineers, Inc., Erie, PA), each equipped with cooling coils and heaters. Cobalt polysulfide catalysts were prepared from cobaltous chloride or cobaltous sulfate, sodium sulfide, and sulfur as reported.[5] The propargyl and 3-methyl-1-hexyn-3-yl esters of 4-nitrobenzoic acid were prepared from the respective alcohols and 4-nitrobenzoic acid as reported.[17] NMR spectra were obtained on a Varian T-60 spectrometer. Shifts are quoted in δ units, parts per million, relative to Me_4Si. A typical procedure involved placing the substrate, catalyst, and solvent into a reactor and hydrogenating under given temperature until the theoretical amount of hydrogen had been consumed (monitored by pressure drop). After depressuring, the reaction mixture is filtered to recover the catalyst, and then solvent is removed on a rotary evaporator to give the product as the residue. (3-Aminophenyl)acetylene was recovered from the residue by vacuum distillation using a simple 6-in. Vigreux column: bp 78–80 °C (0.2 mmHg); n^{20}_D 1.6186; NMR (CCl_4) 3.0 (s, 1, C≡CH), 3.6 (s, 2, NH_2), 6.3–7.2 (m, 4, ring). 2-Methyl-4-(3-aminophenyl)-3-butyn-2-ol was obtained by crystallization from toluene: mp 117–120 °C; NMR ($CDCl_3$) 1.56 (s, 6, CH_3), 3.8–4.6 (s, 3, NH_2, OH, exchanges with D_2O), 6.6–7.2 (m, 4, ring); MS (*m/e*) 157 $(M - H_2O)^+$, 117 $(M - \text{acetone})^+$, but no parent ion. Propargyl 4-aminobenzoate was recovered by crystallization from toluene: mp 88–91 °C; NMR (acetone-d_6) 2.95 (m, 1, C≡CH), 4.9 (d, 2, CH_2), 5.4 (s, 2, NH_2), 6.7 (d, 2, ring), 7.8 (d, 2, ring). 3-Methyl-1-hexyn-3-yl 4-aminobenzoate was obtained as an oil; NMR (acetone-d_6) 0.9 (t, 3, CH_3), 1.1–2.1 (m, 7, CH_2, CH_3), 2.95 (s, 1, C≡CH), 5.5 (s, 2, NH_2), 6.7 (d, 2, ring), 7.8 (d, 2, ring).

Acknowledgment. The authors are grateful to T. P. Debies for the ESCA analyses of ruthenium sulfide catalysts.

Registry No. I, 3034-94-4; II, 33432-52-9; III, 54757-78-7; IV, 71316-81-9; (3-aminophenyl)acetylene, 54060-30-9; 2-methyl-4-(3-aminophenyl)-3-butyn-1-ol, 69088-96-6; propargyl 4-aminobenzoate, 71316-82-0; 3-methyl-1-hexyn-3-yl 4-aminobenzoate, 71316-83-1; ruthenium(IV) sulfide, 12166-20-0.

(17) G. F. Hennion and S. O. Barrett, *J. Am. Chem. Soc.*, **79**, 2146 (1957).
(18) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry", Reinhold, New York, 1961, p 707.
(19) We thank one of the referees for pointing out that low frequency numbers could also be explained by gradual poisoning of cobalt sulfide catalyst.

Influence of the Cyano Group on Orientation of Nucleophiles to Aryne. 1. Reaction of Isomeric Halobenzonitriles with Alkali Amides in Liquid Ammonia[1a]

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Received April 12, 1978

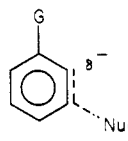
The reaction of either *o*- or *m*-bromobenzonitrile with 2 equiv of lithium amide, sodium amide, or potassium amide yields aminobenzonitriles in a ratio of 95:5 meta/ortho, respectively. Similarly, *p*-bromobenzonitrile gives aminobenzonitriles in a ratio of 80:20 para/meta, respectively. These ratios are in a range which would be expected for the cyano group influencing amination orientation to aryne by the inductive mode. In the presence of 4 equiv of potassium amide, the meta/ortho and para/meta aminobenzonitrile ratios obtained from the corresponding bromobenzonitrile are 89:11 and 95:5, respectively. These altered ratios do not reflect a change in the orienting effect of the cyano group, but rather the instability of the aminobenzonitriles in highly basic medium. Similar results are observed for the reaction of the isomeric iodobenzonitrile with the exception of *o*-iodobenzonitrile, which is predominantly reduced by alkali amide. The reaction of the isomeric chloro- and fluorobenzonitriles yield aminobenzonitrile in very low yields, the predominant product being the corresponding chloro- or fluorobenzoamidine. An explanation in terms of the relative rates of formation of aryne and amidine is presented.

The direction of amination to arynes can be predicted usually by considering the nucleophile to add so as to provide, in the transition state, the most favorable location of the developing negative charge with respect to the inductive effect of the substituent.[2] For example, amination of 3-arynes possessing –I groups (electron withdrawing by induction), such as $-OCH_3$, –Cl, and $-CF_3$, occurs essentially at the 1-position to yield *m*-amino aromatics. Comparison of the transition states for 1- and 2-additions (**1** and **2**, respectively) indicates that the developing negative charge, being closer to the –I substituent

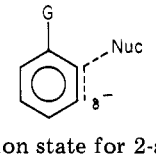
(1) (a) Supported in part by Grant N-118 from Robert A. Welch Foundation, Houston, Texas. (b) Robert A. Welch predoctoral Fellow. (c) Robert A. Welch Undergraduate Scholar.

(2) J. D. Roberts, C. W. Vaughan, L. A. Carlsmith, and D. A. Semenow, *J. Am. Chem. Soc.*, **78**, 611 (1956).

0022-3263/79/1944-3674$01.00/0



transition state for 1-addition
1



transition state for 2-addition
2

in **1** than in **2**, is stabilized inductively to a greater extent by these substituents in **1** than in **2**.

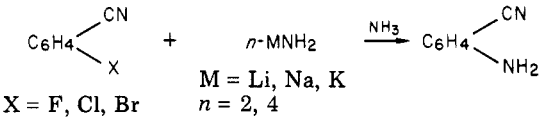
Roberts[2] has suggested that rationalization of orientation to 4-arynes may not be predictable in a straightforward manner, since the inductive effects of the substituent are less strong and the conjugative electronic effects of groups like $-OCH_3$ may become relatively more important. For example, 4-methylbenzyne gives *m*- and *p*-toluidines in the ratio of approximately 1.5:1, which is qualitatively in accord with the electrical effect of the methyl group. However, roughly equal amounts of *m*- and *p*-anisidines are formed from 4-methoxybenzyne.

Stiles[3] and co-workers have observed similar para/meta isomer ratios for 4-fluoro- (3.5:1) and 4-nitrobenzyne (3.8:1) even though these two substituents have different inductive effects; Taft polar substituent constant values[4] are 1.4 for nitro and 1.1 for fluorine. They proposed that the resonance and inductive effects of the nitro group opposed each other, while those of the fluorine atom reinforced each other in polarizing 4-aryne.

deGraaff[5] et al. found that the aminobenzonitrile para/meta ratio, 95–100:5–0, surpasses considerably the fluoroaniline para/meta ratio, 75–80:25–20, obtained from the reactions of potassium amide in liquid ammonia with *p*-bromobenzonitrile and *p*-bromofluorobenzene, respectively. Since the cyano and fluorine substituents have similar –I effects,[4] the distinct preference of *p*-aminobenzonitrile from *p*-bromobenzonitrile seems to be inadequately explained by induction alone. The cyano group appears also to influence nucleophilic addition to 3-arynes, in part, by a noninductive mode. For example, a significantly higher ortho/meta amine isomer ratio (10–15:90–85) is obtained from *o*-bromobenzonitrile than that (0–1:100–99) from *o*-bromofluorobenzene.[5]

Subsequently, Bunnett[6] and Biehl[7] have demonstrated that isomer distributions in certain aryne reactions are dependent upon base concentration. Thus, chloroanisole para/meta isomer distributions from the reaction of 4-chlorobenzyne in neutral methanol was between 4.2 and 6.3 and between 1.8 and 2.6 in 2 M methanolic sodium methoxide. Similarly, the aminobenzoic acid meta/para ratio from the reaction of *p*-chlorobenzoic acid with alkali amide in ammonia changed from 85:15 to 75:25 as the amide ion concentration was changed from 1.5×10^{-3} M (sodium amide solubility in liquid ammonia) to 1.7 M (potassium amide solubility in liquid ammonia).[7]

These results raise the question: Are previously reported abnormal isomer distributions from aryne reactions accountable, in part, for this base dependency? Accordingly, the reaction of isomeric halobenzonitriles under aryne-forming conditions was reinvestigated using saturated liquid ammonia solutions of lithium amide or sodium amide or solutions of potassium amide of varying concentrations. The wide differences in solubility of these



X = F, Cl, Br M = Li, Na, K n = 2, 4

three bases in liquid ammonia allow one conveniently to vary amide ion concentration in this manner. Also, the aryne reaction of *m*-halobenzonitriles has not been reported. These meta isomers can, in principle, give rise to two aryne intermediates, i.e., 3- and 4-cyanobenzynes. A study of the nature of halogen on the distribution of these intermediates would be of interest.

Experimental Section

Materials. Isomeric chloro-, bromo-, and aminobenzonitriles were purchased from Aldrich Chemical Co., *p*-iodobenzonitrile was secured from Eastman Organic Chemicals, and isomeric fluorobenzonitriles were obtained from ICN Corp. *o*- and *m*-iodobenzonitriles were prepared by dehydration of the corresponding iodobenzamide with thionyl chloride in DMF at 0 °C.[8] *o*- and *m*-iodobenzamides[9] and *m*-aminobenzamidine[10] were synthesized by literature methods. The purity of halo and amino compounds was checked by GLC or LC analysis. Liquid ammonia was purchased from Van Waters and Associates, Dallas, Texas; potassium, sodium, and lithium metals were obtained from J. T. Baker.

Equipment. Spectral characteristics were determined on the following instruments: infrared spectra (IR), Perkin-Elmer Model 457; proton nuclear magnetic resonance spectra (^{1}H NMR), Perkin-Elmer Model 32 (90 mHz) using Me_4Si as standard (δ 0); mass spectra (MS), duPont Dimaspec Model 521 GC/MS with 70-eV ionizing voltage and equipped with a 4 ft × $^1/_4$ in. glass column packed with 3 % OV-17 on Supelcoport 80/100 (Supelco, Inc.). Analytical high-pressure liquid chromatography (LC) was carried out on Waters liquid chromatograph Model ALC/GPC-244 and gas chromatographic analysis was performed on a Hewlett-Packard Model 5830A gas chromatograph equipped with electron capture detector (ECD).

General Procedure. The alkali amide was prepared in situ by the addition of the appropriate alkali metal to 50 mL of anhydrous ammonia containing a few crystals of ferric nitrate. Then the appropriate halobenzonitrile was added in portions over a period of 30 s to a stirred suspension, in the case of lithium amide or sodium amide, or to a stirred solution, in the case of potassium amide. After the appropriate reaction time had elapsed, an equivalent amount of ammonium chloride, based upon the quantity of alkali amide, was added and the ammonia was evaporated on a steam bath.

Isomeric aminobenzonitriles were isolated by stirring reaction residue with 40 mL of methylene chloride for 15 min, filtering, transferring mother liquor to a 50-mL volumetric flask, and diluting to volume with additional methylene chloride. Qualitative identification of aminobenzonitriles in methylene chloride extract was accomplished by comparing R_f values and mass spectra obtained by GC/MS analysis to those of authentic samples. Quantitative analysis of aminobenzonitrile was done by LC using a 3.9 mm i.d. × 30 cm μ-Porasil column, 95:5 (vol/vol) methylene chloride/acetonitrile solvent system at 1.0 mL/min flow rate and UV detector set at 254 nm. R_f values of aminobenzonitriles under these conditions are 4.0, 4.5, and 5.0 min for meta, ortho, and para isomers, respectively. Percentage yield of each isomer was determined using *p*-dibromobenzene as internal standard.

The methylene chloride insoluble residue was stirred with 50 mL of methanol for 15 min and the resulting mixture was filtered. Concentration of the mother liquid (rotary evaporator) yielded in all reactions an intractable tar. LC analysis of these tars was done using a 4.6 mm i.d. × 25 cm Zorbax C8-850 column (duPont), 35:65 (vol/vol) water/methanol solvent system at a 1.0 mL/min flow rate, and UV detector set at 254 nm. A complex chromatogram was obtained from all reaction tars. GC analysis using

(3) M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).
(4) H. H. Jaffe, *Chem. Rev.*, **53**, 206 (1953).
(5) G. B. R. deGraaff, H. J. den Hertog, and W. C. Melger, *Tetrahedron Lett.*, 963 (1965).
(6) J. F. Bunnett, D. A. R. Happer, M. Patsch, C. Pyun, and H. Takayama, *J. Am. Chem. Soc.*, **88**, 5250 (1966).
(7) E. R. Biehl, E. Nieh, H. Li, and C. Hong, *J. Org. Chem.*, **34**, 500 (1969).
(8) J. C. Thurman, *Chem. Ind. (London)*, 752 (1964).
(9) I. Remsen and E. E. Reid, *Am. Chem. J.*, **21**, 289 (1899).
(10) A. Pinner and N. Caro, *Ber. Dtsch. Chem. Gas.*, **28**, 468 (1895).

EC detector, 4 ft × $^1/_4$ in. glass column packed with 3% OV-101 on Chromosorb Q 80/100, and a temperature program of 290–350 °C over a 30-min range indicates that/several of the compounds in the tarry mixture contain halogen. Most of the chromatographic bands eluted during the last 10 min of the run (330–350 °C). Infrared indicates the absence of nitrile and the presence of C=N bands in the tarry residue.

Direct probe mass spectroscopy of a small portion of the solid residue indicated in certain cases the presence of benzamidine, aminobenzamidines, and/or halobenzamidines. These products were identified on the basis of their mass spectra and were not quantitated.

Reaction of Isomeric Aminobenzonitrile with Potassium Amide. A 0.01-mol (1.18 g) sample of a particular isomeric aminobenzonitrile was treated with 0.04 mol of potassium amide (2.2 g) in the same manner described in the general method, using a reaction time of 5 min. The residue after evaporation of ammonia was found to contain the corresponding aminobenzamidine by mass spectral analysis: *m/e* 135, which corresponds to molecular ion, and a peak at 119 which corresponds to the $NH_2C_6H_4C^+{=}NH$ ion. In addition, several other unidentified products were observed as indicated by LC and IR analysis. The retention volume and retention times corresponded to several of those observed in the chromatograms of the reaction mixture from the reaction of isomeric halobenzonitriles with alkali amides.

Results and Discussion

The results from the reaction of halobenzonitriles with 2 equiv of lithium amide, sodium amide, or potassium amide or 4 equiv of potassium amide are presented in Table I. These reactions essentially went to completion in 5 min, even those in which the weakest and least soluble alkali amide, lithium amide, was used.

Ortho and meta isomers of bromo- and iodobenzonitriles gave *m*- and *o*-aminobenzonitriles in the same ratio, i.e., ca. 95:5 meta/ortho respectively, when reacted with 2 equiv of lithium amide. Also, para isomers of bromo- and iodobenzonitrile similarly treated were converted to *p*- and *m*-aminobenzonitriles in identical ratios, 75:25 para/meta, respectively.

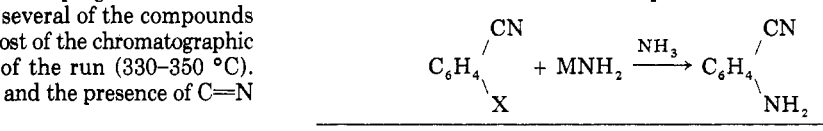
These meta/ortho or para/meta ratios are in the range of those observed from amination of 3- and 4-arynes possessing other strong –I substituents, such as F (100:0 meta/ortho, 80:20 para/meta).[5] However, aminobenzonitrile isomer distributions similar to those reported by deGraaff[5] (89:11 meta/ortho, 95:5 para/meta) were obtained from reactions in which 4 equiv of potassium amide were used.

The yields of aminobenzonitriles from *o*- and *m*-bromobenzonitriles dropped markedly from 74–84% to 23–38% as the alkali amide was changed from lithium amide to either sodium amide or potassium amide. *p*-Bromobenzonitrile gave aminobenzonitriles in good yields (80–87%) when treated with 2 equiv of any one of the three aforementioned alkali amides; however, a lower yield (55%) of aminobenzonitriles was obtained with 4 equiv of potassium amide. An intractable tar was isolated from those reactions in which the yields of aminobenzonitriles were less than 74%. GC, IR, MS, and LC indicated these tars to be complex mixtures containing isomeric aminobenzamidines, the corresponding bromobenzamidines as well as many other compounds which appear to be dimers, trimers, etc., resulting from nucleophilic addition between bromo and amino derivatives of both benzonitrile and benzamidines. In separate reactions, each one of the three isomeric aminobenzonitriles was treated with 4 equiv of potassium amide and found to give intractable tars. Several of the components of the aminobenzonitrile reaction tars had the same retention volume (LC) or retention time (GC) as several of those in the bromobenzonitrile reaction tars. An assessment of the amount of each initially formed aminobenzonitrile which reacts further under highly basic conditions cannot be made due to the myriad products formed in these reactions. However, the change in the aminobenzonitrile isomer distribution with change in base concentration most likely reflects the instability of these amines in highly basic media. These results indicate that the cyano group influences orientation to aryne in the usual sense, namely, by induction; electronic conjugative effects need not be invoked.

o-Iodobenzonitrile is primarily metalated to benzonitrile, which is aminated, in part, to benzamidine under the basic conditions used in this study. Aminobenzonitrile yields from *o*-iodobenzonitrile were too low to allow an accurate determination of amine isomer distribution, with the exception of the lithium amide reaction. In addition, intractable tars were obtained from the reaction of all the isomeric iodobenzonitriles, except that of *p*-iodobenzonitrile and lithium amide. GC, LC, MS, and IR indicates these tars to be complex mixtures similar to that observed in the bromobenzonitrile reaction.

Chloro- or fluorobenzonitriles were converted predominantly to the corresponding chloro- or fluorobenzoamidine regardless of the alkali amide used. This explains the seemingly paradoxical behavior of the weakest base, $LiNH_2$, giving the highest yields of aryne product in comparison to the stronger bases, $NaNH_2$ and KNH_2. Significant yields of aminobenzonitriles were obtained only

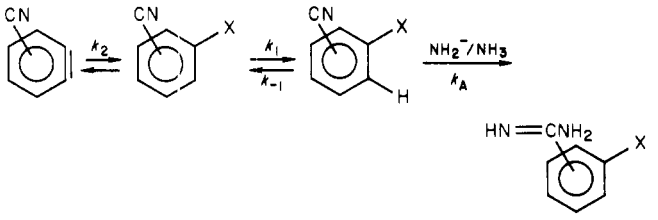
Table I. Reaction of Isomeric Halobenzonitriles with Alkali Amide in Liquid Ammonia[a]



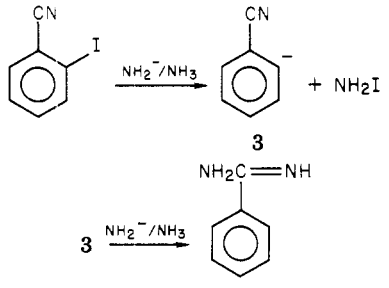
			aminobenzonitriles		
	MNH_2			isomer ratio	
X	M	*n*	yield, %	m/o	p/m
o-Br	Li	2	84	96:4	
	Na		38[b]	94:6	
	K		36[b]	96:4	
	K	4	27[b,c]	89:11	
m-Br	Li	2	74	96:4[h]	
	Na		33[b]	94:6[h]	
	K		38[b]	94:6[h]	
	K	4	23[b,c]	89:11[h]	
p-Br	Li	2	84		78:22
	Na		87		75:25
	K		80		76:24
	K	4	55[c]		95:5
o-I	Li	2	31[d]	95:5	
	Na		3[d]	*e*	
	K		3[d]	*e*	
m-I	Li	2	44	96:4	
	Na		40	95:5	
	K		37	95:5	
o-I	Li	2	76		75:25
	Na		60		76:24
	K		50		73:27
	K	4	25[c]		96:4
o- and *p*-Cl[f]					
m-Cl	Li	2	8		75:25
	Na		10		75:25
	K		14		79:21
o, *m*, and *p*-F[g]					

[a] Five-min reaction time. [b] Corresponding halobenzamidine detected. [c] *m*-Aminobenzamidine detected. [d] Benzamidine detected. [e] Yields too low to determine accurately. [f] Corresponding chlorobenzamidines major product. [g] Corresponding fluorobenzamidine major product. [h] Trace amounts of *p*-aminobenzonitrile were detected.

Scheme I



Scheme II

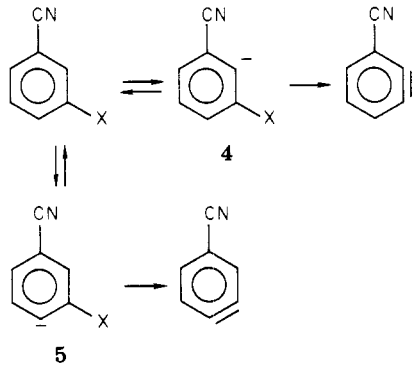


from the reaction of *m*-chlorobenzonitrile with 2 equiv of alkali amide. Interestingly, this *m*-chloro isomer gave an aminobenzonitrile para/meta ratio of 75:25, which is the same observed for *p*-bromobenzonitrile and 2 equiv of base; *o*-aminobenzonitrile was not detected.

Scheme I illustrates two pathways available to halobenzonitriles under aryne-forming conditions. One pathway involves direct attack of amide ion onto nitrile to yield the benzamidine derivative and the other proceeds through aryne intermediates. For X = Br and I (with the exception of *o*-iodo), the latter pathway appears to predominate; for X = Cl and F, the former seems to prevail. The rate of metalation of aryl halides with alkali dialkylamide in the presence of free base, dialkylamine, is known to decrease along the series X = Br > I > Cl > F.[11] A similar trend would be expected for metalations conducted in liquid ammonia. In addition, the rate of amidine formation, which increases with increasing electronegativity of the substituent group present in the nitrile derivative, follows the series X = F > Cl > Br > I.[12] The composite of these factors explains the observed results: bromo- and iodobenzonitriles, with the exception of the *o*-iodo isomer, yield aminobenzonitrile and chloro- and fluorobenzonitriles produce halobenzamidine.

The mechanism for the metalation of *o*-iodobenzonitrile, shown in Scheme II, is similar to that proposed for metalation of haloanisoles under aryne-forming conditions.[13]

Scheme III



The formation of *p*- and *m*-aminobenzonitrile from *m*-chlorobenzonitrile indicates that only 4-cyanobenzyne is generated. Bunnett[14] has observed previously that 4-chlorobenzyne is produced predominantly from *m*-dichlorobenzyne by potassium amide in liquid ammonia. Also, the obtention of all three isomeric aminobenzonitriles from *m*-bromobenzonitrile indicates that the two possible aryne intermediates, 3- and 4-cyanobenzynes, are produced. The very small yield of *p*-aminobenzonitrile indicates that 3-cyanobenzyne is produced to a much larger extent than 4-cyanobenzyne. Aryne formation from these *m*-halobenzonitriles should occur mainly by abstraction of the 2-proton, which is the most acidic, to form the 2-halo-6-cyanophenyl anion (**4**), which then would lose halide ion to form 3-cyanobenzyne. Alternatively, abstraction of the less acidic 4-proton to form the 2-halo-4-cyanophenyl anion (**5**), which would lose halide ion to form 4-cyanobenzyne, may compete with the former pathway. These two pathways are shown in Scheme III. In the case of *m*-chlorobenzonitrile, the unexpected pathway to 4-cyanobenzynes occurs exclusively, since the energy content and hence tendency to lose chloride ion is greater for anion **5** than for anion **4**. The greater tendency of bromo anion **4** to lose bromide ion as compared to the chloro derivative results in the formation of the expected 3-cyanobenzyne from *m*-bromobenzonitrile in a much higher yield than the unexpected 4-cyanobenzyne.

Registry No. *o*-Bromobenzonitrile, 2042-37-7; *m*-bromobenzonitrile, 6952-59-6; *p*-bromobenzonitrile, 623-00-7; *o*-iodobenzonitrile, 4387-36-4; *m*-iodobenzonitrile, 69113-59-3; *p*-iodobenzonitrile, 3058-39-7; *o*-chlorobenzonitrile, 873-32-5; *p*-chlorobenzonitrile, 623-03-0; *m*-chlorobenzonitrile, 766-84-7; *o*-fluorobenzonitrile, 394-47-8; *m*-fluorobenzonitrile, 403-54-3; *p*-fluorobenzonitrile, 1194-02-1; *o*-aminobenzonitrile, 1885-29-6; *m*-aminobenzonitrile, 2237-30-1; *p*-aminobenzonitrile, 873-74-5; *o*-aminobenzamidine, 4392-06-7; *m*-aminobenzamidine, 3459-66-3; *p*-aminobenzamidine, 3858-83-1; *o*-chlorobenzamidine, 45743-05-3; *p*-chlorobenzamidine, 19563-04-3; *o*-fluorobenzamidine, 71204-93-8; *m*-fluorobenzamidine, 69491-64-1; *p*-fluorobenzamidine, 2339-59-5.

(11) R. Huisgen and J. Sauer, *Chem. Ber.*, **92**, 192 (1959).
(12) F. C. Schaeffer and A. P. Krapcho, *J. Org. Chem.*, **27**, 1255 (1962), and references cited therein.
(13) E. R. Biehl, S. Lapis, and P. C. Reeves, *J. Org. Chem.*, **39**, 1900 (1974).
(14) J. A. Zoltewicz and J. F. Bunnett, *J. Am. Chem. Soc.*, **87**, 2640 (1965).